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Anionic Transition Metal Hydrides

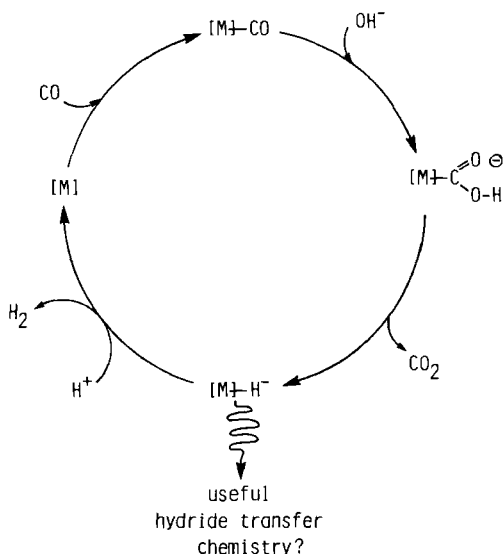
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I

INTRODUCTION

The motives for studies and a review of the anionic transition metal hydrides are varied. Rowland Pettit best expressed the idea that interruption of the water-gas shift reaction cycle (Scheme 1) at the point of the anionic hydride should find an activated hydride reagent capable of delivering H^- to a reducible substrate (1). That is, with certain reducible substrates, particularly those containing polar bonds, a distinct H^-/H^+ delivery system should offer



SCHEME 1. Water-gas shift reaction cycle.

¹ Present address: Phillips Petroleum Company, Bartlesville, Oklahoma 74004.

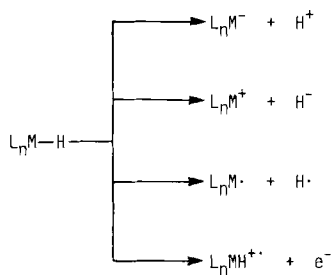
advantages over concerted hydrogen addition. A significant part of this article is devoted to the scope and reactivity of anionic transition metal hydrides with organic substrates.

A large portion of homogeneous catalytic processes (2) of import to the reduction of unsaturated organics, the reduction and homologation of oxycarbon compounds, and the use of carbon monoxide as a reducing agent have as catalysts, catalyst precursors, or mechanistically required intermediates anionic transition metal hydride complexes. Such "electron-rich" hydrides should not only be highly reactive and of interest in their own right, but should also serve as models for the electronic environment of hydrogen, dissociatively adsorbed on a catalytically active metal surface. The latter is particularly appropriate for those metal catalysts that are further activated by doping with alkali metals which serve to donate electrons into the Fermi level of the metal catalyst.

In a more fundamental vein, the hydride ligand enjoys an unmatched structural and chemical versatility in coordination chemistry. It can act as a terminal ligand, it can serve to bridge two metal centers, even in the absence of supporting bridging ligands or M—M bonds, and it can bridge three or more M—M bonded centers. It is both inter- and intramolecularly mobile. The reactivity patterns known for the metal hydride functional group are similarly diverse.

As indicated in Scheme 2, there are discrete metal hydride complexes which are acidic [e.g., $\text{HCo}(\text{CO})_4$, a strong acid (3)] as well as hydridic [e.g., Cp_2ZrH_2 (4) and *cis*- $\text{HW}(\text{CO})_4\text{PMe}_3^-$ (5)] in character, undergoing heterolytic M—H cleavage reactions. The homolytic M—H cleavage is appropriate to many reactions, and there is also much evidence of single electron transfer from M—H bonds.

The reactivity pattern exercised by a particular $[\text{M}-\text{H}]$ is influenced by the central metal, the ancillary ligands, and by the substrate. As example of



SCHEME 2

substrate dependencies, HMn(CO)_5 is described as a weak acid (6), ionizing in aqueous media obviously with the assistance of substantial hydrogen bonding. With very strong acids such as HOSO_2CF_3 the hydrogen in HMn(CO)_5 reacts as H^- , yielding H_2 and $\text{Mn(CO)}_5(\text{CF}_3\text{SO}_3)$ (7). Similarly the Mn(CO)_5^+ species is produced on reaction of HMn(CO)_5 and AlBr_3 , producing $[\text{Mn(CO)}_5]\text{AlBr}_4$ and $\text{Mn(CO)}_5\text{Br}$ (8). Homolytic cleavage of the Mn-H bond has been convincingly demonstrated in the hydrogenation of α -methylstyrene by HMn(CO)_5 (9).

The possibility of heterolytic cleavage yielding H^+ and ML_n^- should be substantially reduced in anionic complexes of metal hydrides. (Nevertheless, proton abstraction *can* be effected in strongly basic media and provides a convenient route to subreduced organometallic compounds.) The remaining reaction path possibilities in Scheme 2 present complicated mechanistic problems. Additionally, in reactions of metal hydrides with electrophiles, E^+ , one might anticipate yet another pathway involving oxidative addition and reductive elimination [Eq. (1)]. A discussion of metal-based nucleophilicity such as demonstrated in Eq. (1) versus hydride-ligand-based nucleophilicity is presented later in this article.

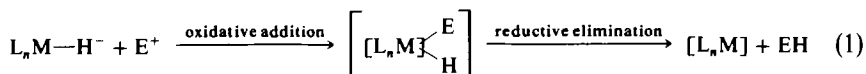


Table I lists anionic transition metal hydrides which are covered in this article. They are in general tractable; i.e., they are soluble, with good spectroscopic handles, and of known reaction chemistry. The intractable anionic polyhydrides are neglected, as are also (because of space limitation) anionic cluster hydrides. An overview of spectroscopic and structural features of monomeric and dimeric anionic hydrides is presented as prelude to a more extensive discussion of reactivity.

The well-known reviews of transition metal hydride complexes such as the monograph edited by E. L. Muetterties in 1972, *Transition Metal Hydrides* (10), and the *Chemical Reviews* article by H. Kaesz and R. B. Saillant, "Hydride Complexes of the Transition Metals," published in 1972 (11), contain few anionic hydrides. The development of synthetic techniques in the 1970s and the growing interest in modelling catalytic processes yielded many studies of anionic transition metal hydrides. By 1982 when the New York Academy of Sciences hosted a conference entitled "Catalytic Transition Metal Hydrides" (12), a large number of presentations included catalytic cycles requiring anionic hydrides. Nevertheless, to our knowledge, this is the first review which addresses the unique properties of anionic transition metal complexes containing the hydride ligand.

TABLE I
SPECTROSCOPIC PROPERTIES OF TRANSITION METAL ANIONIC HYDRIDES^a

Entry	Compound	$\delta(\text{H}^-)$ (ppm)	Solvent	Coupling constants, J	$\nu(\text{CO})$ or $\nu(\text{MH})$ (cm^{-1})	Solvent	Reference
Category 1. CO-containing, mononuclear, monohydrides							
5-1	$[\text{Et}_4\text{N}]_2 \text{HV}(\text{CO})_5$				1905,1700	Nujol	13
5-2	$\text{Na}_2 \text{HV}(\text{CO})_5$	-4.76	NH_3	$\text{VH} = 27.6$			13
5-3	$[\text{Et}_4\text{N}]_2 \text{HNb}(\text{CO})_5$				1923,1700	Nujol	13
5-4	$\text{Na}_2 \text{HNb}(\text{CO})_5$	-1.89	NH_3	$\text{NbH} \approx 80$			13
5-5	$[\text{Et}_4\text{N}]_2 \text{HTa}(\text{CO})_5$				1922,1700	Nujol	13
5-6	$\text{Na}_2 \text{HTa}(\text{CO})_5$	-2.23	NH_3				13
5-7	$[\text{PPN}] \text{CpV}(\text{CO})_3\text{H}$	-6.72	THF		1887,1775	THF	14
5-8	$[\text{Et}_4\text{N}] \text{CpV}(\text{CO})_3\text{H}$	-6.33		$\text{VH} = 20.3$	1889,1775	MeCN	15
5-9	$[\text{Et}_4\text{N}] \text{CpNb}(\text{CO})_3\text{H}$	-5.6	MeCN	$\text{NbH} \approx 36$	1900,1789	MeCN	16
5-10	$\text{Na CpNb}(\text{CO})_3\text{H}$				1897,1799,1739	THF	17
	$[\text{R}_n\text{M}']^+/\text{Na CpNb}(\text{CO})_3\text{H}$						
5-11	$[\text{R}_n\text{M}'] = \text{Ph}_3\text{Ge}$				1903,1815,1760	THF	17
5-12	$[\text{R}_n\text{M}'] = \text{Ph}_3\text{Sn}$				1897,1806,1759	THF	17
5-13	$[\text{R}_n\text{M}'] = \text{Et}_3\text{Sn}$				1887,1800,1750	THF	17
5-14	$[\text{R}_n\text{M}'] = \text{Ph}_3\text{Pb}$				1909,1820,1770	THF	17
5-15	$[\text{R}_n\text{M}'] = \text{Et}_3\text{Pb}$				1894,1869,1812	THF	17
6-1	$^+[\text{PPN}] \text{HCr}(\text{CO})_5$	-6.73	THF		2017,1883,1852	THF	18
6-2	$[\text{PPN}] \text{DCr}(\text{CO})_5$	-6.84	THF		2017,1882,1853	THF	18
6-3	$[\text{PPN}] \text{HMo}(\text{CO})_5$	-4.0	MeCN		2030,1893,1858	THF	18c,19
6-4	$[\text{PPN}] \text{HW}(\text{CO})_5$	-4.10	THF	$\text{WH} = 52.5$	2029,1888,1856	THF	18
6-5	$[\text{PPN}] \text{DW}(\text{CO})_5$	-4.09	THF	$\text{WD} = 8.0$	2030,1887,1855	THF	18
6-6	$[\text{Et}_4\text{N}] \text{H}(\text{Ph}_3\text{Sn})_2\text{Cr}(\text{CO})_4$	-4.9	MeCN		1989,1960,1891	MeCN	20
6-7	$[\text{Et}_4\text{N}] \text{H}(\text{Ph}_3\text{Sn})_2\text{W}(\text{CO})_4$	-2.5	MeCN	$\text{WH} = 10.8$	2008,1919,1903	MeCN	20
7-1	$[\text{Et}_4\text{N}] \text{CpRe}(\text{CO})_2\text{H}$	-12.35	MeCN		1846,1770	THF	21
7-2	$\text{K CpRe}(\text{CO})_2\text{H}$	-12.38	MeCN		1859,1775,1760	THF	21
7-3	$[\text{PPN}] \text{HRe}(\text{CH}_3)(\text{CO})_4$	-5.56	THF				14a
7-4	$[\text{PPN}] \text{HRe}(\text{COCH}_3)(\text{CO})_4$	-4.38	THF				14a
8-1	$^+[\text{PPN}] \text{HFe}(\text{CO})_4$	-8.68	THF		1995,1905,1876	THF	22,23
8-2	$[\text{PPN}] \text{DFe}(\text{CO})_4$				1994,1888,1875	THF	22

8-3	[PPN] HRu(CO) ₄	-7.77	Me ₂ CO		2003,1927,1885	THF	22
8-4	[PPN] DRu(CO) ₄				1999,1906,1884	THF	22
8-5	[PPN] HOs(CO) ₄	-10.15	Me ₂ CO		2008,1945,1881	THF	22
8-6	[PPN] DOs(CO) ₄				2003,1904,1881	THF	22
10-1	[Na(THF) ₄] HNi(CO) ₃	-8.3	THF		2009,1954	THF	24
10-2	[Ph ₄ As] HPd(CO)Cl ₂				1900		25
Category 2. Phosphine derivatives of Category 1 anions							
6-8	[PPN] HCr(CO) ₄ P(OMe) ₃	-7.00	THF	PH = 54	1971,1854,1817	THF	18
6-9	[PPN] HW(CO) ₄ P(OMe) ₃	-4.35	THF	PH = 36, WH = 54	1982,1855,1821	THF	26,18
		-4.5	MeCN	PC = '41.6, °7&11			
6-10	[PPN] HW(CO) ₄ PPh ₃	-3.0	MeCN	PH = 27	1974,1851,1815	THF	26
6-11	[PPN] HW(CO) ₄ PMe ₃	-3.6	MeCN	PH = 30, WH = 54	1969,1847sh,1842,1805	THF	26
8-7	[PPN] HFe(CO) ₃ P(OMe) ₃	-9.20	THF (22°C)	PH = 11.9	1941,1841	THF	27
8-8	[PPN] HFe(CO) ₃ P(OEt) ₃	-9.10	THF (22°C)	PH = 4.84	1938,1836	THF	27
8-9	[†] [Et ₄ N] HFe(CO) ₃ PPh ₃	-9.12	THF (22°C)	PH = 12.0	1927,1831,1813	THF	27
8-10	[Et ₄ N] HFe(CO) ₃ PPh ₂ Me	-9.17	THF (22°C)	PH = 8.77	1924,1828,1810	THF	27
8-11	[Et ₄ N] HFe(CO) ₃ PMe ₃	-9.46	THF (22°C)	PH = 3.77	1919,1821,1805	THF	27
8-12	[Et ₄ N] HFe(CO) ₃ PEt ₃	-9.33	THF (22°C)	PH = 3.24	1917,1817,1802	THF	27
Category 3. Non-CO-containing, mononuclear, monohydrides							
6-12	[†] [K(cr)] HMoCp ₂	-7.74	THF				28
6-13	[μ-(H ₁₁ C ₆)MgBr ₂ Mg(OEt ₂)] ₂ HMo(Cp) ₂						29
8-13	K ⁺ (HRuOEP) ⁻	-57.04	THF				30
8-14	[Et ₃ NH] HOs(PF ₃) ₄						31
9-1	K ₃ HCo(CN) ₅	-12.65	H ₂ O		1860	HBr	32
9-2	K ₃ HRh(CN) ₅	-10.61	H ₂ O	HC = '56.2, °5.7			32
9-3	K ₃ HIr(CN) ₅	-14.37	H ₂ O	HC = '37.2, °5.7			32
10-3	[Me ₄ N] HPt(SnCl ₃) ₄				2072,2052	Me ₂ CO	33
10-4	[Et ₄ N] HPt(SnCl ₃) ₂ (PEt ₃) ₂				2108	MeOH	33
10-5	[Me ₄ N] HPt(GeCl ₃) ₅				2083	KBr	34
10-6	M ⁺ Me ₃ Al—H—Ni(C ₂ H ₄) ₂	-4.80	THF				24

(continued)

TABLE I (continued)

Entry	Compound	δ (H ⁺) (ppm)	Solvent	Coupling constants, <i>J</i>	ν (CO) or ν (MH) (cm ⁻¹)	Solvent	Reference
10-7	M ⁺ Et ₃ Ga—H—Ni(C ₂ H ₄) ₂	−4.55	THF				24
12-1	Li H[ZnR ₂] _x (x = 1, 2)	+5.4–+6.0			1650–1250	Nujol	35
Category 4. Binuclear monohydrides							
5-16	Na μ -H[CpNb(CO) ₃] ₂				1850,1812	THF	16
5-17	[PPN] μ -H[CpV(CO) ₃] ₂				1857,1817	THF	14c
6-13	[†] [PPN] μ -HCr ₂ (CO) ₁₀				2013,1940,1879	THF	36
6-14	[†] [PPN] μ -DCr ₂ (CO) ₁₀						36
6-15	[†] [K(crypt)] μ -HCr ₂ (CO) ₁₀				2033,1942,1875	CH ₂ Cl ₂	37
6-16	Na μ -HCr ₂ (CO) ₁₀	−19.17	THF		2032,1942,1879	THF	38
6-17	[†] [Et ₄ N] μ -HCr ₂ (CO) ₁₀	−19.47	THF		2033,1943,1881	THF	38,36,18
6-18	[†] [PPN] μ -HMo ₂ (CO) ₁₀						39
6-19	Na μ -HMo ₂ (CO) ₁₀	−12.15	THF	HC = '?, °4.3	2044,1946,1881	THF	31,38
6-20	[Et ₄ N] μ -HMo ₂ (CO) ₁₀	−12.2	THF		2041,1941,1877	THF	40,38,18
6-21	Na μ -HW ₂ (CO) ₁₀	−12.58	THF	HC = '4.3, °3.5 WH = 42.1	2041,1941,1879	THF	38,31
6-22	[†] [Et ₄ N] μ -HW ₂ (CO) ₁₀	−12.60	THF		2043,1943,1880	THF	38,41,18,42
6-23	[†] [PPN] μ -HW ₂ (CO) ₁₀				2041,1940,1879	THF	41
6-24	[†] [Ph ₄ P] μ -HW ₂ (CO) ₁₀						41
6-25	Na μ -HCrMo(CO) ₁₀	−15.31	THF		2030,2000,1930,1870,1830	THF	38
6-26	[Et ₄ N] μ -HCrMo(CO) ₁₀	−15.47	MeCN		2032,1948,1884	THF	18
6-27	Na μ -HMoW(CO) ₁₀	−12.37	THF	HC = 4.0, WH = 42.3	2035,1930,1875	THF	38
6-28	Na μ -HCrW(CO) ₁₀	−15.43	THF		2030,2010,1930,1870,1830	THF	38
6-29	[Et ₄ N] μ -HCrW(CO) ₁₀	−15.60	MeCN		2039,1946,1886	THF	18
6-30	[†] [Et ₄ N] μ -HMo ₂ (CO) ₉ PPh ₃	−11.10		PH = 20	2053,2001,1928,1875,1840	THF	43
6-31	[PPN] μ -HW ₂ (CO) ₉ P(OMe) ₃	−12.20	MeCN	PH = 25.8 W ¹ H = 42, W ² H = 45.6	2054,2002,1931,1879,1851	THF	26
6-32	[PPN] μ -HCrW(CO) ₉ P(OMe) ₃	−14.4	MeCN	PH = 27,	2047,2002,1931,1882,1850	THF	26

6-33	[PPN] μ -H[W(CO) ₄ P(OMe) ₃] ₂	-11.8	MeCN	WH = 38.4 PH = 21	2019,1997,1912,1882,1838	THF	26
6-34	[Et ₄ N] μ -H[W(CO) ₄ PMe ₃] ₂	-11.2	MeCN	WH = 40.8, PH = 16	1998,1980,1887,1867,1827	MeCN	44
6-35	[Et ₄ N] μ -H[W(CO) ₄ PMe ₂ Ph] ₂	-10.8	MeCN	WH = 44.0, PH = 15.6	2000,1984,1897,1873,1823	THF	44
6-36	[†] [Et ₄ N] μ -H[Mo(CO) ₄ PMePh ₂] ₂	-11.75	Me ₂ CO	PH = 16.6	2021,1989,1906,1875,1822	THF	45
7-5	[Et ₄ N] HRe ₂ (CO) ₉	-7.10	Me ₂ CO		2078,2028,1972,1924,1888	THF	46
8-15	[†] [PPN] μ -HFe ₂ (CO) ₈				1987,1940,1880,1852,1770	THF	47
8-16	[Na(cr)] μ -HFe ₂ (CO) ₈	-9.01	THF		1987,1940,1880,1852,1770	THF	47
8,6-1	[PPN] HFeCr(CO) ₉	-13.4	THF		2057,2012,2000, 1942,1911,1880	THF	48
8,6-2	[PPN] HFeW(CO) ₉	-11.8	THF	WH = 15.0	2063,2009,1940,1911,1870	THF	48
8,6-3	[Et ₄ N] Me ₃ P(CO) ₃ HFeW(CO) ₅	-12.6	THF	PH = 26.3, WH = 14.3	2053,2039,1918,1888,1842	THF	48
8,6-4	[PPN] ⁺ (MeO) ₃ P(CO) ₃ HFeCr(CO) ₅ ⁻	-15.3	THF	PH = 22.5	2050,2035,1956,1929, 1897,1870,1851	THF	48
8,6-5	[PPN] (CO) ₄ FeHW(CO) ₄ PPh ₃	-13.4	THF	PH = 23.1, WH = 33.0	2028,1996,1921 1893,1873,1843	THF	48
10-8	[†] [PPN] μ -HNi ₂ (CO) ₆	-8.6			2005,1950	THF	49
10-9	M ⁺ μ -HNi ₂ (C ₂ H ₄) ₄	-8.3-9	THF				24
Category 5. CO-containing anionic polyhydrides							
6-37	K ₂ H ₂ W(CO) ₄	-3.4	MeCN	WH = 33.6	1851,1837,1729,1704	HMPA	44
6-38	Li ₂ H ₂ W(CO) ₄				1842,1744,1730	MeCN	44
6-39	[Et ₄ N] ₂ H ₂ Cr ₂ (CO) ₈	-14.6	MeCN		1958,1877,1825,1789	MeCN	44
6-40	[Et ₄ N] ₂ H ₂ Mo ₂ (CO) ₈	-7.7	MeCN		1976,1887,1831,1797	MeCN	44
6-41	[Et ₄ N] ₂ H ₂ W ₂ (CO) ₈	-4.5	Me ₂ CO	WH = 30.4	1976,1884,1829,1800	MeCN	44,50
6-42	[†] [PPN] ₂ H ₂ W ₂ (CO) ₈	-4.72	MeCN	WH = 32	1970,1878,1824,1797	MeCN	51
7-6	[†] [Et ₄ N] H ₂ Re(CO) ₄	-7.0	Me ₂ CO		2020,1995,1930,1895	CH ₂ Cl ₂	52
7-7	[Et ₄ N] H ₃ Re ₂ (CO) ₆	-17.49	MeCN		1995,1905	MeCN	53
8-17	H ₃ Fe(CO) ₃ ⁻						54

(continued)

TABLE I (continued)

Entry	Compound	$\delta(\text{H}^-)$ (ppm)	Solvent	Coupling constants, J	$\nu(\text{CO})$ or $\nu(\text{MH})$ (cm^{-1})	Solvent	Reference
Category 6. Non-CO-containing anionic polyhydrides							
4-1	$\text{Li Cp}_2\text{TiH}_2$						55
6-43	$[\text{Na}(\text{cr})] \text{H}_5\text{W}(\text{PMe}_3)_3$	-5.1, -5.9	THF (25°C)	PH = 35, 21			56
6-44	$\text{Na H}_5\text{W}(\text{PMe}_3)_3$	-4.3, -5.8, -6.1	THF (-73°C)				56
6-45	$^t[\text{K}(\text{cr})] \text{H}_5\text{W}(\text{PMe}_3)_3$	-4.3, -5.2, -6.2	THF (-70°C)	PH = 23			56
6-46	$\text{K H}_5\text{W}(\text{PMe}_3)_3$	-4.7, -5.5, -5.7	THF (-98°C)	PH = 21.7			56
6-47	$[\text{Li H}_5\text{W}(\text{PMe}_3)_3]_4$	-4.6, -6.0, -7.1	THF (-135°C)				
		-5.6	THF (50°C)				56
7-8	$\text{K}_2 \text{TcH}_9$	-8.4	$\text{OH}^-/\text{H}_2\text{O}$		1869,1795,1779	KBr	57d
7-9	$^t\text{K}_2 \text{ReH}_9$	-9.1	$\text{OH}^-/\text{H}_2\text{O}$		1931,1846,1814	KBr	57
7-10	$[\text{Et}_4\text{N}]_2 \text{ReH}_9$	-8.5	MeCN				58
7-11	$[\text{Et}_4\text{N}] \text{H}_8\text{RePEt}_3$	-8.2	MeCN	PH = 17.3	1980,1920,1850	KBr	58
7-12	$[\text{Et}_4\text{N}] \text{H}_8\text{RePBu}_3$	-8.1	MeCN	PH = 18.4	1980,1920,1850	KBr	58
7-13	$[\text{Et}_4\text{N}] \text{H}_8\text{RePPh}_3$	-7.3	MeCN	PH = 17.7	1980,1940,1860	KBr	58
7-14	$[\text{Et}_4\text{N}] \text{H}_8\text{AsPh}_3$	-7.4	MeCN		1980,1940,1850	KBr	58
7-15	$\text{K H}_6\text{Re}(\text{PMePh}_2)_2$	-7.96	THF	PH = 15	1938,1872,1842	Nujol	59
8-18	$^t\text{K}(\text{Ph}_3\text{P})_2\text{Ph}_2\text{PC}_6\text{H}_4\text{RuH}_2$	-7.0, -11.0	THF	PH = 81, 27, 21, HH = 6 PH = 19, 81, 19, HH = 6	1825,1735	Nujol	60
8-19	$\text{K}_2(\text{Ph}_3\text{P})_3(\text{Ph}_2\text{P})\text{Ru}_2\text{H}_4$	-13.0, -13.7, -15.6, -16.8	THF	PH = 37, 42	1830,1775,1745	Hexadecane	60
8-20	$\text{K H}_3\text{Ru}(\text{PPh}_3)_3$	-9.53	THF		1857,1815	Nujol	61
8-21	$\text{K HRu}(\text{PPh}_3)_2(\text{anthracene})$	-14.1	THF	PH = 24	1850	Nujol	61
8-22	$\text{K H}_5\text{Ru}(\text{PPh}_3)_2$	-7.64	THF	PH = 15	1750	Nujol	61
8-23	$\text{K H}_3\text{Ru}(\text{PPh}_3)_2$	-13.4, -8.08	THF	PH = 21, HH = 7			61
8-24	$^t[\text{K}(\text{cr})] \text{H}_3\text{Ru}(\text{PPh}_3)_3$						62
8-25	$\text{Li H}_3\text{Ru}(\text{PPh}_3)_3$						62
8-26	$^t\text{K H}_3\text{Os}(\text{PMe}_2\text{Ph})_3$	-11.88	Toluene				63

^a Abbreviations used: t, trans; c, cis; M⁺, alkali cations; crypt, cryptand; cr, 15-crown-5 or 18-crown-6; OEP, octaethylporphyrin. A dagger preceding the compound signifies that an X-ray or neutron crystal structure determination has been carried out.

II

STRUCTURAL CHARACTERISTICS

Table I lists anionic transition metal hydrides along with vibrational [$\nu(\text{CO})$ and $\nu(\text{MH})$] and proton magnetic resonance spectral features. The table is arranged by categories: (1) CO-containing, mononuclear, monohydrides; (2) Phosphine derivatives of Category 1 anions; (3) Non-CO-containing, mononuclear, monohydrides; (4) Binuclear monohydrides; (5) CO-containing anionic polyhydrides; and (6) Non-CO-containing anionic polyhydrides. In most solid state structure determinations the hydride ligand was not directly located by X-ray methods, due to the typical problem of the low scattering ability of hydrogen. In those cases ligand angle deformations are taken as an indication of the hydride position. The few neutron diffraction studies that were done on anionic hydrides were involved with the problem of linear versus bent $\text{M}-\text{H}-\text{M}$ bonding in $\mu\text{-HM}_2(\text{CO})_{10}$ ($\text{M} = \text{group 6}$) salts (found in Table I, Category 4).

The known solid state structures of anionic hydrides all indicate stereoactivity of the hydride ligand, and that stereoactivity is apparently similar to that of the hydride ligand in isoelectronic neutral analogs. This point is illustrated in Fig. 1, where structural comparisons are made between three anionic hydrides and their neutral counterparts [the latter structures were determined from electron diffraction measurements (64)]: $\text{HCr}(\text{CO})_5^-$ and $\text{HMn}(\text{CO})_5$; $\text{H}_2\text{Re}(\text{CO})_4^-$ and $\text{H}_2\text{Fe}(\text{CO})_4$; $\text{HFe}(\text{CO})_4^-$ and $\text{HCo}(\text{CO})_4$. All show distortions of the coordination sphere so as to relax the CO ligands into the space provided by the smaller steric requirement of the hydride ligand. Salient features of the structure of $\text{Ph}_4\text{P}^+\text{HCr}(\text{CO})_5^-$ (18a) are as follows: The $\text{Cr}-\text{H}$ bond distance is 1.66(5) Å, the Cr is displaced out of the equatorial-CO plane towards the trans-CO by 0.176 Å, and there are only minor differences between the $\text{Cr}-\text{C}$ bonds in $\text{Cr}-(\text{CO})_{\text{trans}}$ versus $\text{Cr}-(\text{CO})_{\text{cis}}$ [1.852(4) and 1.865(3), respectively].

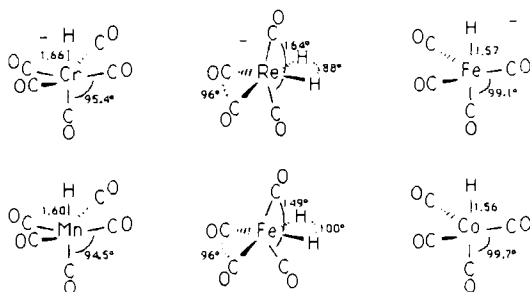
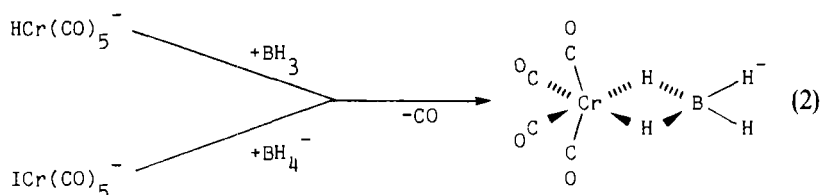


FIG. 1. Comparison of structures of isoelectronic anionic and neutral metal carbonyl hydrides.

The hydride ligands in octahedral $\text{H}_2\text{Re}(\text{CO})_4^-$ are *cis*, with $\angle \text{H—Re—H}$ of 88° (52). Thus the plane containing the two hydrides and the equatorial carbonyls shows little distortion from regular octahedral geometry, whereas the axial carbonyls bend in toward the hydrides with a $\angle \text{C}_{\text{ax}}\text{—Re—C}_{\text{ax}}$ of 164° . As indicated in Fig. 1, there is apparently much more distortion in the neutral $\text{H}_2\text{Fe}(\text{CO})_4$ analog (64). Our understanding that M—H bonds are stronger for heavier metals, coupled with an expectation that the anionic charge in $\text{H}_2\text{Re}(\text{CO})_4^-$ is somewhat localized on the hydrides, leads to the reasonable conclusion that the hydride ligands in $\text{H}_2\text{Re}(\text{CO})_4^-$ have a more distinct stereoactivity than in $\text{H}_2\text{Fe}(\text{CO})_4$. We caution that this conclusion has not been tested on a range of hydrides. An interesting contrast is with $\text{Cr}(\text{CO})_4(\mu\text{-H})_2\text{BH}_2^-$, synthesized as in Eq. (2). The constrained steric

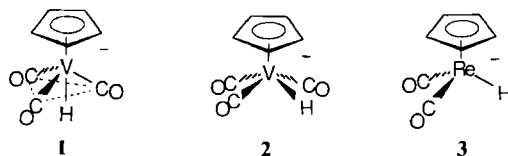


requirement of the $(\mu\text{-H})_2\text{BH}_2^-$ bidentate ligand [$\angle \text{H—Cr—H} = 58(3)^\circ$] allows the equatorial carbonyls to expand to a $\text{C}_{\text{eq}}\text{—Cr—C}_{\text{eq}}$ of $94.8(4)^\circ$; however, the axial CO groups actually move *away* from the hydride ligation sites with a $\text{C}_{\text{ax}}\text{—Cr—C}_{\text{ax}}$ of $175.6(4)^\circ$ (18*b*). The Mo analog is isostructural (65).

Structures of anionic $\text{HFe}(\text{CO})_4^-$ (23) and neutral $\text{HCo}(\text{CO})_4$ (64) (Fig. 1) may be viewed as proton attack along one face of tetrahedral $\text{Fe}(\text{CO})_4^{2-}$ or $\text{Co}(\text{CO})_4^-$, respectively, resulting in identical distortions toward trigonal bipyramidal geometry. This view is further supported by the structure of $\text{Me}_3\text{NH}^+\text{Co}(\text{CO})_4^-$ which also finds the $\text{Co}(\text{CO})_4^-$ in C_{3v} symmetry with the Me_3NH^+ occupying an expanded face of (what was) T_d $\text{Co}(\text{CO})_4^-$ (66). In solution the proton is evidently migrating between the metallo-base and the amine. The chemical shift for the hydrogen of -8.1 ppm indicates the hydrogen to be metal bound on the average.

Phosphine-substituted derivatives of $\text{HFe}(\text{CO})_4$ are known, and the X-ray crystal structure of $\text{Et}_4\text{N}^+\text{HFe}(\text{CO})_3\text{PPh}_3^-$ has been carried out (27). The PPh_3 ligand is *trans* to hydrogen in the trigonal bipyramidal (or H-capped tetrahedral) anion. Despite the huge bulk of PPh_3 , the steric requirement of the hydride ligand maintains the P—Fe—C angle of *trans*- $\text{HFe}(\text{CO})_3\text{PPh}_3^-$ at the same value as the $\text{OC}_{\text{ax}}\text{—Fe—CO}_{\text{eq}}$ in $\text{HFe}(\text{CO})_4^-$, i.e., $99.5(3)^\circ$ versus $99.1(30)^\circ$, respectively. In a series of eight P-substituted derivatives, only *one* was found to be a *cis*-configuration as confirmed by X-ray crystallography: *cis*- $\text{HFe}(\text{CO})_3\text{P}(\text{OPh})_3^-$ (27*a*).

Since the five-coordinate hydrides appear to be equally well described as a distorted trigonal bipyramid or as a H-capped tetrahedron, one might expect the seven-coordinate hydrides of the formula $\text{CpM}(\text{CO})_3\text{H}^-$ ($\text{M} = \text{V}, \text{Nb}$; Entries 5-7 to 5-10, Table I) to be a face-capped octahedron. In fact, Puttfarcken and Rehder (15) have suggested, on basis of V-51 to H coupling and relaxation times, that the local symmetry of $\text{V}(\text{CO})_3\text{H}$ is C_{3v} , i.e., a $(\text{CO})_3$ face of the $\text{CpV}(\text{CO})_3$ "octahedron" is capped by H, structure 1. Alternatively,

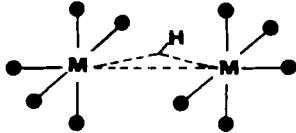
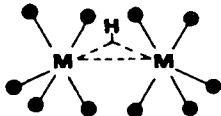


structure 2, a four-legged piano stool (i.e., the H caps a mixed Cp—CO face of the $\text{CpV}(\text{CO})_3$ "octahedron"), was proposed by Bergman and co-workers (14) in analogy to the NMR-established geometry of $\text{CpW}(\text{CO})_3\text{H}$ (67). Certainly low barriers to site exchange are expected for structure 2; Faller *et al.* estimated the barrier for $\text{CpW}(\text{CO})_3\text{H}$ to be approximately 10–13 kcal/mol and proposed the 3:3:1 structure (analogous to 1) to be an intermediate in the site exchange (67). The structure of $\text{CpRe}(\text{CO})_2\text{H}^-$ is doubtless a three-legged piano stool, 3 (21). Crystal structures are not available for either $\text{CpV}(\text{CO})_3\text{H}^-$ or $\text{CpRe}(\text{CO})_2\text{H}^-$.

Category 4 of Table I contains a series of binuclear hydrides which have been extensively studied by X-ray and neutron diffraction methods: $\mu\text{-HM}_2(\text{CO})_{10}^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and derivatives. The extreme interest in these hydrides stems from attempts to understand both the strength and the flexibility of the unsupported M—H—M bridge. Observed are variable configurations or conformers depending on M, on counterion and crystal-packing influences, and on substituent ligands. The structural possibilities may be defined according to the linearity (or lack thereof) of the intersecting vectors $\text{OC}_{\text{ax}}\text{—M}\cdots\text{M—CO}_{\text{ax}}$ and the relative orientation of equatorial carbonyls on each metal center (eclipsed or staggered). Of the possible combinations, the bent, staggered structure 5 predominates by far in the known solid state determinations (Table II). The second most common structure is of the linear, eclipsed form, which is observed for Et_4N^+ salts of $\mu\text{-HM}_2(\text{CO})_{10}^-$ structures (41a).

Although early workers concluded the $\mu\text{-HCr}_2(\text{CO})_{10}^-$ was less susceptible than its congeners toward a bent, staggered configuration, possibly because of attractive van der Waals interactions between equatorial CO groups (68), more recent studies have found counterion effects which promote the deformation from structure 4 to 5. The salt $\text{K}^+\mu\text{-HCr}_2(\text{CO})_{10}^-$ showed three crystallographically independent sites for the anions, two belonging to the

TABLE II
SUMMARY OF STRUCTURES OF $\mu\text{-HM}_2(\text{CO})_{10}^-$ AND DERIVATIVES^a

 <p>4</p> <p>Linear, eclipsed</p>		 <p>5</p> <p>Bent, staggered</p>	
Compound	M...M (Å)	Compound	M...M (Å)
$\text{K}^+\text{HCr}_2(\text{CO})_{10}^-$	3.343(3) (69)	$\text{K}^+\text{HCr}_2(\text{CO})_{10}^-$	3.260(3) (69)
	3.260(3)	$\text{PPN}^+\text{HMo}_2(\text{CO})_{10}^-$	3.422(1) (39)
	and 3.356(3) (69)	$[\text{K}\cdot\text{crypt-222}]^+\text{HMo}_2(\text{CO})_{10}^-$	3.406(1) (39)
$^\dagger\text{Et}_4\text{N}^+\text{HCr}_2(\text{CO})_{10}^-$	3.386(6) (36a)	$\text{Et}_4\text{N}^+\text{HMo}_2(\text{CO})_9\text{PPh}_3$	3.474(1) (43)
$^\dagger\text{PPN}^+\text{HCr}_2(\text{CO})_{10}^-$	3.349(13) (36b)	$\text{Et}_4\text{N}^+\text{HMo}_2(\text{CO})_8(\text{PMePh}_2)_2^-$	3.443(1) (43)
$^\dagger\text{PPN}^+\text{DCr}_2(\text{CO})_{10}^-$	3.390(3) (36c)	$\text{cat}^+\text{HMo}_2(\text{CO})_8[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]^-$	
$\text{Et}_4\text{N}^+\text{HW}_2(\text{CO})_{10}^-$	3.528(2) (41a)	cat ⁺ = Ph_4P^+ , $n = 1$	3.4028(8) (70)
		cat ⁺ = Et_4N^+ , $n = 4$	3.4995(8) (70)
		$^\dagger\text{Ph}_4\text{P}^+\text{HW}_2(\text{CO})_{10}^-$	3.340(5) (41c)
		$\text{PPN}^+\text{HW}_2(\text{CO})_{10}^-$	3.391(1) (41b)
Compound	M...M (Å)		
$^\dagger[\text{K}(\text{crypt-222})]^+\text{HCr}_2(\text{CO})_{10}^-$	3.300(4) (37)		

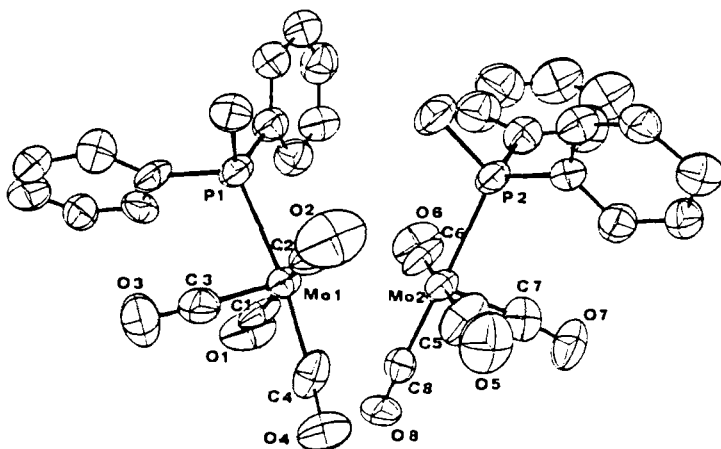
^a A dagger preceding a compound signifies that a neutron crystal structure determination has been carried out.

linear, eclipsed type and the third being the first example of a bent, staggered $\mu\text{-HCr}_2(\text{CO})_{10}^-$ unit (69). Clear evidence for $\text{K}^+ \cdots ^-\text{OC}-\text{Cr}$ interactions [$\text{K}^+ \cdots \text{O}$ contact distances of 2.72(1) and 2.77(1) Å] to the two axial carbonyl oxygens of the bent, staggered anion was noted. The bend in the $\text{OC}_{\text{ax}}-\text{Cr} \cdots \text{Cr}-\text{CO}_{\text{ax}}$ backbone was 165° , the $\text{Cr}-\text{H}-\text{Cr}$ angle was 132° , and the staggering of the independent sets of equatorial carbonyls was about 36° .

Encapsulated in a cryptand ligand, the interaction of $[\text{K}(\text{crypt}\cdot 222)]^+$ with an equatorial CO oxygen of $\mu\text{-HCr}_2(\text{CO})_{10}^-$ is predictably less perturbing of the anion (37). The intersection of the two projected $\text{OC}_{\text{ax}}-\text{Cr}$ vectors is 169° , and the two $\text{Cr}(\text{CO})_5$ units are rotated by an average 19° angle with respect to one another about the $\text{Cr} \cdots \text{Cr}$ axis.

In all cases where analogous linear, eclipsed and bent, staggered structures are known, the configurational change is accompanied by a diminishing of $\text{M}-\text{M}$ distance. For example, the $\text{W} \cdots \text{W}$ separation in linear, eclipsed $\text{Et}_3\text{NH}^+ \mu\text{-HW}_2(\text{CO})_{10}^-$ is 3.528(2) Å whereas in $\text{Ph}_4\text{P}^+ \mu\text{-HW}_2(\text{CO})_{10}^-$, of structural type 5, that distance decreases by almost 0.2 Å (41c). For the $\mu\text{-HCr}_2(\text{CO})_{10}^-$ series discussed above the decrease is only about 0.1 Å. The change is also accompanied by a similar decrease in $\text{M}-\text{H}-\text{M}$ angle. For the $\mu\text{-HCr}_2(\text{CO})_{10}^-$ studies, structural type 4 has a $\angle \text{Cr}-\text{H}-\text{Cr}$ of $150\text{--}160^\circ$, and in type 5 that angle is 132° . All known $\text{M}-\text{H}-\text{M}$ angles in type 5 anions are in the $125\text{--}140^\circ$ range.

The extent of staggering of the independent $\text{M}(\text{CO})_5$ or $\text{M}(\text{CO})_4\text{L}$ units of $\mu\text{-HM}_2(\text{CO})_8\text{L}$ ($\text{L} = \text{CO}, \text{PR}_3$) is dependent both on counterion and on L.



Already noted was the counterion effect of K^+ and $[K \cdot \text{crypt-222}]^+$ on $\mu\text{-HCr}_2(\text{CO})_{10}^-$, leading to twist angles of 36 and 19°, respectively. The average twist angle in $\mu\text{-HMo}_2(\text{CO})_8(\text{PMePh}_2)_2^-$ (in which the PMePh_2 ligands are located as shown in structure 6) is 43° (45).

The exo positions of the two PMePh_2 ligands in 6 suggested that they might be replaced by bidentate ligands. In fact, the X-ray crystal structures of $(\mu\text{-H})[\mu_2\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]\text{Mo}(\text{CO})_8^-$ (70) showed a subtle positioning of the two bridges, rationalized by the inherent stability of the bent, staggered configuration of the $\mu\text{-HM}_2(\text{CO})_{10}^-$ anions. Figure 2 represents the starting material, $\mu\text{-HMo}_2(\text{CO})_{10}^-$, in its bent, staggered structure. Examination of molecular models and calculation of coordination site position separations in the all-carbonyl parent suggested that the large bite distance of $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ could best be accommodated by its occupancy of sites 2 and 9, i.e., exo positions, over the top of the Mo-H-Mo bridge as was observed. In contrast, the best fit of the $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ bite to coordination site position was apparently between positions 4 and 7, i.e., underneath the Mo-H-Mo bridge. In fact, the observation of "cis" site occupancy as indicated for the dppm ligand leads to perpendicular bridge planes. As amplified in Fig. 3, the staggering angle is greatly dependent of the bridge ligand; however, the framework bends ($\sim 160^\circ$) and Mo-H-Mo angles ($\sim 132^\circ$) are the same for both structures.

As implied by the difference in framework bend and M-H-M angles, the

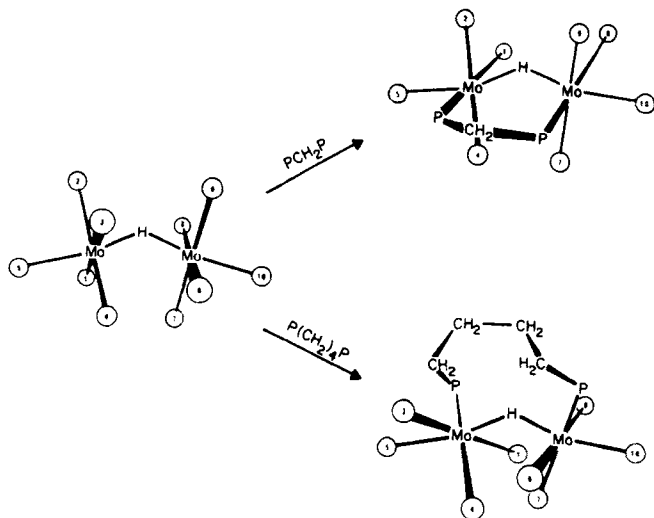


FIG. 2. Stick drawings of the coordination site positions in $(\mu\text{-H})\text{Mo}_2(\text{CO})_{10}^-$. [Taken from the ORTEP plot of the $\text{PPN}^+(\mu\text{-H})\text{Mo}_2(\text{CO})_{10}^-$ (39) and derived molecular structures (45).]

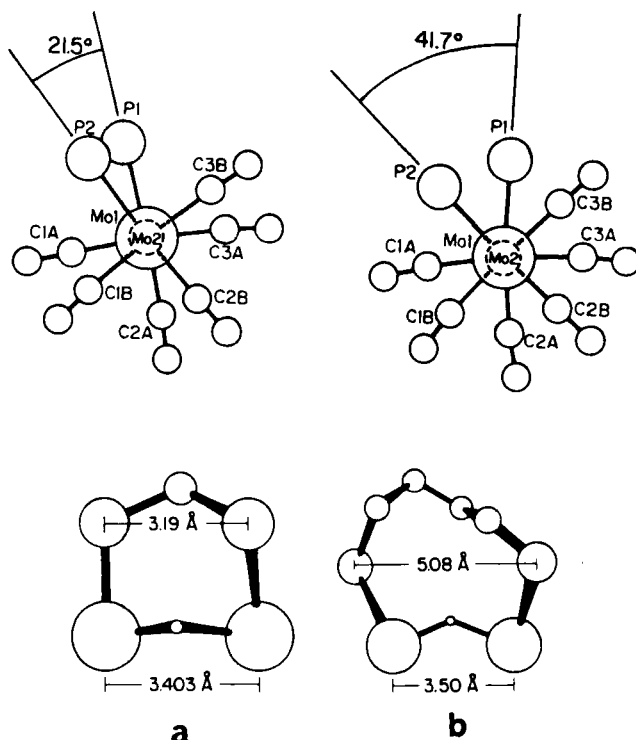
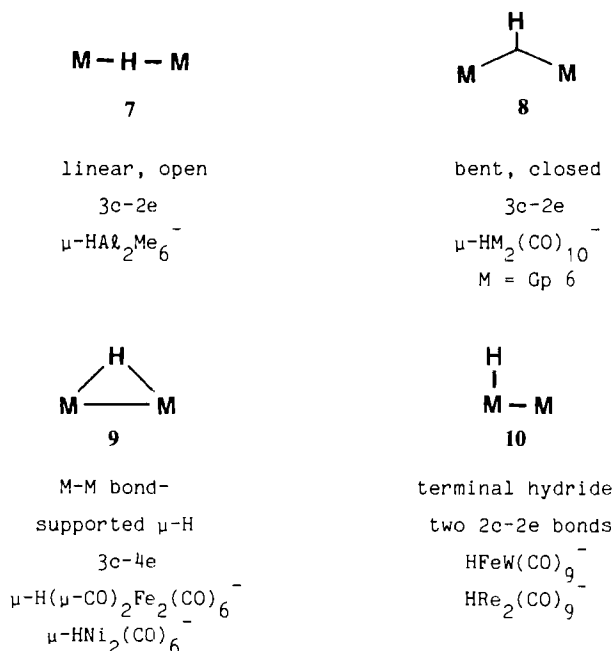


FIG. 3. (Top) Views of $\mu\text{-HMo}_2(\text{CO})_6[\mu\text{-Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2]^-$ along the Mo—Mo bond showing degree of staggering for $n = 1$ (a) and $n = 4$ (b). (Bottom) Views of corresponding $(\mu\text{-H})(\mu\text{-PP})\text{Mo}_2$ bridges (45).

hydride ligand is offset from the point of intersection of the projected independent $\text{OC}_{\text{ax}}\text{—M}$ vectors (Scheme 3, structure 8) in all known $\mu\text{-HM}_2(\text{CO})_{10}^-$ ($\text{M} = \text{Group 6}$) anions. The bridge bond is described as a closed, three-center, two-electron bond (41a). The extent of the closed character of the bond, or metal—metal interaction, is small in general and increases slightly in the type 5 (Table II) structural forms. The original controversy about the possibility of a linear hydride bridge (68), structure 7, has not been realized for group 6 metal carbonyl hydrides. As indicated in Scheme 3, the main group binuclear hydride, $\text{H}[\text{AlMe}_3]_2^-$, has a linear Al—H—Al arrangement with insignificant metal—metal interaction ($\text{Al}\cdots\text{Al} = 3.30 \text{ \AA}$) and Al—H distances of 1.65 \AA (71). The short M—M distances in structures of $\text{HFe}_2(\text{CO})_8^-$ (11) (47) and $\text{HNi}_2(\text{CO})_6^-$ (12) (49) [$2.521(1)$ and $2.864(3) \text{ \AA}$, respectively] indicate a M—M bond supports the hydride bridge as in Scheme 3, type 9.



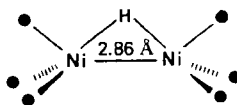
SCHEME 3. Bonding of the hydride ligand in bimetallic complexes.

Asymmetric hydride bridges are observed for inherently asymmetric dimers such as $\mu\text{-H}[\text{Mo}(\text{CO})_5][\text{Mo}(\text{CO})_4\text{PPh}_3]^-$ in which the $\text{Mo}-\text{H}$ distance to the more electron-rich Mo center, $\text{Mo}(\text{CO})_4\text{PPh}_3$, is considerably longer than that to the more electron-poor $\text{Mo}(\text{CO})_5$ [2.19(6) versus 1.68(5) Å, respectively] (43). Asymmetry is expected in the $\mu\text{-H}[\text{MM}'(\text{CO})_{10}]^-$ anions ($\text{M} \neq \text{M}' = \text{Group 6}$) (38b,72); however, as yet no solid state structures have been determined.

In even more asymmetric binuclear hydrides, as in the heterobimetallics $\text{HFeM}(\text{CO})_9^-$ ($\text{M} = \text{group 6}$), the hydrogen ligand is almost certainly a terminal hydride, located on iron (48,73). X-Ray structure analyses were unable to locate the hydride in these anions; however, bond angle deformations and the similarity of the structure of the analogous Ph_3PAu derivative (74) (Fig. 4) was convincing evidence of the existence of structural



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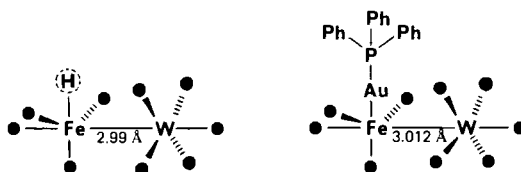
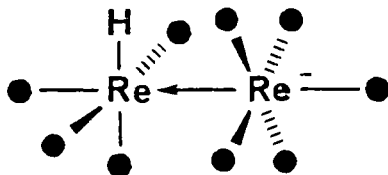


FIG. 4. Comparisons of X-ray structures of the HFeW(CO)_9^- (hydrogen placed in expected, not located, position) (73) and the isolobal analog $\text{Ph}_3\text{PAuFeW(CO)}_9^-$ (74).

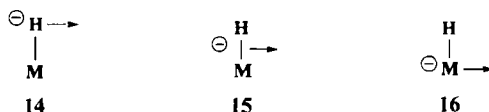
type 10, Scheme 3. The hydride affinity of iron, as compared to that of the Group 6 metals, coupled with the achievement by Fe of a favorable coordination geometry [TBP $\text{HFe(CO)}_4^- \rightarrow \text{Oh } \text{H(OC)}_4\text{Fe}^- \rightarrow \text{W}$] and electron configuration ($d^8 \rightarrow d^6$), rationalizes the structure (75).

Interestingly the homobimetallic hydride $\text{HRe}_2(\text{CO})_9^-$ has been established by NMR (46a) and by X-ray analysis (46b) to be also of structural type 10. Based on our analysis of the donor-acceptor nature of the $\text{Fe} \rightarrow \text{M}$ bond in HFeM(CO)_9^- anions, it is expected that in $\text{HRe}_2(\text{CO})_9^-$ there is a reversal of arrangement. Namely, the Re(CO)_5^- moiety is most likely the metallo-donor ligand whereas the HRe(CO)_4 species is the 16-electron acceptor (structure 13).

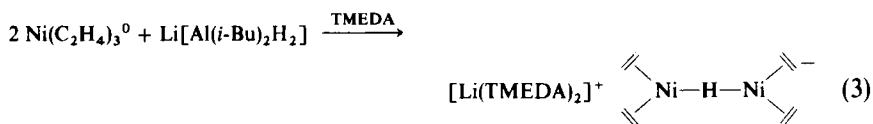


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Another description of the bonding in heterobimetallic hydrides places emphasis on the donor nature of the $\text{M}-\text{H}$ bond density. A gradation of donor site electron density from primarily on hydrogen (for polarization $\text{M}-\text{H}^{\delta-}$) (structure 14), intermediate between hydrogen and M (15), and primarily on metal (for $\text{M}^{\delta-}-\text{H}$) (16) also accounts for the different structural types observed.



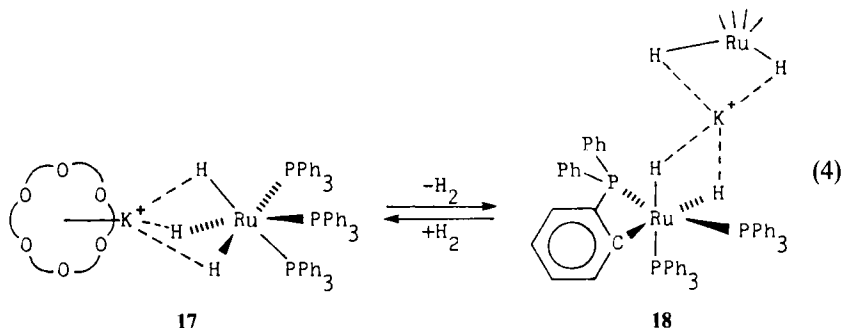
An interesting $\mu\text{-H}$ anionic complex synthesized according to Eq. (3) has been reported (76,77). In analogy to the well-characterized monomeric anion, $\text{MeNi(C}_2\text{H}_4)_2^{2-}$ (77), a trigonal coordination about Ni is proposed.



As indicated in Table I, there are a number of non-carbonyl containing hydrides whose structures are known. The most noteworthy of these are the alkali salts of the polyhydrides which show strong ion pair interaction. For example, Caulton *et al.* suggests the notation $\text{P}_3\text{Os}(\mu\text{-H})_3\text{K}$ to be appropriate for the salt $\text{K}[\text{fac-OsH}_3(\text{PMe}_2\text{Ph})_3]$ (63). The salt is soluble in both THF and toluene (!), and crystallizes in dimeric units which not only show K^+ interactions with two hydride anion units but also an engulfing of K^+ by phenyl rings which renders the molecule lipophilic.

An analogous ruthenate $\text{fac-H}_3\text{Ru}(\text{PPh}_3)_3^-$ has been isolated as its (18-crown-6) K^+ salt (62). The X-ray diffraction study revealed a distorted octahedral disposition of ligands about Ru [structure 17, Eq. (4)]. The K^+ , displaced by 0.75 Å of the average crown ether donor oxygen plane, contacts the anion via the facial RuH_3 , presumably with substantial $\text{K}^+ \cdots \text{H}^{\delta-}$ interactions, similar to the Caulton–Huffman structures described above.

Another structurally characterized anionic ruthenium hydride may be derived from $\text{H}_3\text{Ru}(\text{PPh}_3)_3^-$ upon loss of H_2 and ortho-metallation of one PPh_3 ligand, as formally idealized in Eq. (4). The $\text{K}^+[(\text{Ph}_3\text{P})_2\text{Ph}_2\text{PC}_6\text{H}_4\text{RuH}_2]^-$ salt (18) has unsolvated or nonsequestered K^+ ions which interact simultaneously with two anions via the hydride ligand sites (60).

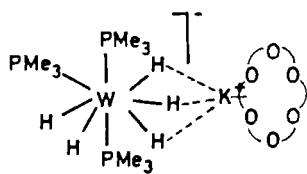
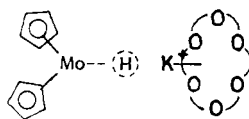


Additional structures demonstrating alkali cation interactions with anionic hydrides strong enough to displace the cation from a plane of donor oxygens in a sequestering crown ether have originated from the Oxford laboratories and include (15-cr-5) Na^+ and (18-cr-6) K^+ salts of $\text{W}(\text{PMe}_3)_3\text{H}_5^-$ as well as (18-cr-6) $\text{K}^+[\text{HMoCp}_2]^-$ (28,56). The Na^+ ion is displaced by 1.10 Å out of the average crown ether donor plane and was at 3.125(6) Å from W in (15-cr-5) $\text{Na}^+\text{W}(\text{PMe}_3)_3\text{H}_5^-$. In that structure the hydride ligands were not

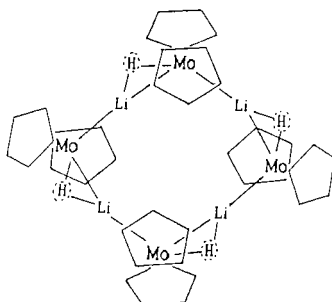
located; however, in the analogous potassium salt (**19**) it was possible to determine $K^+ \cdots H^-$ distances of 2.78 Å (similar to the distance in ionic KH). Interestingly the $W-K^+$ distance of 3.660(1) Å is comparable to the sums of the covalent radii ($K = 1.96$ Å and $W = 1.6$ Å) (56).

The crystal structure of the non-solvated lithium salt of $H_5W(PMe_3)_3^-$ disclosed a tetrameric cluster with alternating distances (2.77 and 2.93 Å) between Li and W, suggesting the presence of μ -H ligands which could not be located by X-ray crystallographic methods (56). It appears that Li^+ is buried in an almost spherical coordination of hydride ligands from two adjacent $H_5WP_3^-$ anions.

As demonstrated by structure **20**, there is also a strong interaction of K^+ with the $HMoCp_2^-$ anion. The K^+ is once again displaced from the 18-cr-6 oxygen donor plane by 0.866 Å. The $Mo-K$ distance of 3.614 Å suggests that the (unlocated) hydride will be found in a two-electron, three-center bonding arrangement.

**19****20**

The $HMoCp_2^-$ unit is also found in the cluster product derived from reaction of Cp_2MoH_2 with BuLi, yielding $[Cp_2Mo(H)Li]_4$ (**21**) (78). Structure **21** depicts the reviewers' representation of the unlocated hydrogen atoms in probable locations. The $Mo-Li$ interaction averages to 2.70 Å in the eight-membered $Mo-Li$ ring, and multicenter or μ -H[$Mo-Li$] arrangements are postulated. Clearly the notion of ionic bonding is suspect in such "salts," and the degree of covalency is expected to increase

**21**

with increasing electrostatic potential of the counterion. As an example, the $V_2Zn_2H_4(BH_4)_2(PMePh)_4$ complex has been described either as V_2Zn_2 aggregate with bridging hydrides or as a $V_2H_4P_4^{2-}$ ion strongly interacting with $Zn(BH_4)^+$ counterions (79).

III

SPECTROSCOPIC PROPERTIES

A. Infrared [$\nu(CO)$ and $\nu(MH)$]

Infrared and nuclear magnetic resonance spectroscopies are the primary tools for analyzing the solution structures of transition metal hydrides. Infrared spectroscopy is especially useful in carbonyl-containing complexes. Analysis of $\nu(CO)$ (carbonyl stretching modes) absorption positions yields information about electronic distribution. Application of the IR selection rules via a group theory approach gives geometrical information. Judicious use of $\nu(CO)$ intensity patterns and band ratios can refine the molecular geometry even to the point of determining angles in solution.

The $\nu(CO)$ band positions are to lower energies for anionic carbonyl hydrides as compared to neutral analogs, illustrating the ability of the CO ligand to delocalize added negative charge. Uninegative monomeric metal hydrides typically have CO stretching vibrations between 2000 and 1800 cm^{-1} , with the major band at approximately 1900 cm^{-1} . The major band for terminal CO groups in uninegative dimeric hydrides is higher, typically 1940–1950 cm^{-1} . Addition of more negative charge via σ -donating ancillary ligands such as phosphines lowers the average $\nu(CO)$ by 10–50 cm^{-1} . The few known dinegative carbonyl hydrides have even lower $\nu(CO)$, in the range of 1900–1700 cm^{-1} . For an analogous series $(OC)_xM-E^-$, the following trend of the energies of the $\nu(CO)$ bands is noted: $E^- = \text{halide}^- > H^- \gtrsim R^-$. This suggests the hydride ligand to be better capable of donating electron density than halide, and approximately equal to R^- .

In all cases known to us (with possible exception of some curious ion-paired structures involving Et_4N^+ counterions) the analysis of $\nu(CO)$ infrared spectra of monomeric carbonyl hydrides has agreed with the anions' geometry as determined by X-ray structure analysis of the solid state. As an example, the X-ray structure of $PPN^+HFe(CO)_4^-$ shows the anion to be a distorted trigonal bipyramid with H in the axial position and an average $OC_{ax}-Fe-CO_{eq}$ angle of 99.1° (23). The $\nu(CO)$ IR spectrum is consistent with a C_{3v} symmetry point group assignment, yielding three IR active CO stretches (A_1^1 , A_1^2 , and E). A more detailed analysis suggested the A_1 sym-

metry species represented by a symmetrical stretch of the equatorial carbonyls is observable (or gains intensity) in three possible ways: (1) by coupling with the axial CO group motion, (2) through departure of the $\text{OC}_{\text{ax}}-\text{M}-\text{CO}_{\text{eq}}$ bond angle from 90° , and (3) by electronic migration along the three fold axis, i.e., a transverse dipole moment change in the $\text{M}-\text{L}$ bond. Since the last contribution arises from motion of π electron density in the $\text{M}-\text{L}$ bond, and can be neglected for $\text{L} = \text{H}^-$, it can be shown that the intensity ratio of A_1^1 to A_1^2 is related to the group MCO dipole moment derivatives and the angle between them. Thus, the $\text{OC}_{\text{ax}}-\text{Fe}-\text{CO}_{\text{eq}}$ was calculated from solution IR intensity data to be 100.2° (80). The same analysis was applied to *trans*- $\text{HFe}(\text{CO})_3\text{PPh}_3^-$ and to $\text{HCr}(\text{CO})_5^-$ with good correlation between solid state and solution angles (72,81).

The metal-hydrogen stretch should also be useful for analysis of the electronic character of a particular anion; however, this vibrational frequency is rarely available due to the fact that it is usually a weak and broad absorption or is obscured by other absorptions such as $\nu(\text{CO})$ bands. The fact that $\nu(\text{MH})$ bands are weak (low intensity) may be attributable to the similar electronegativity of middle to late transition metals and hydrogen, resulting in a relatively nonpolar bond and a small change in dipole as the stretch occurs (82). Terminal metal-hydrogen stretching bands generally occur between 2100 and 1700 cm^{-1} , while bridging hydride bands are found to lower frequencies ($1700-1000\text{ cm}^{-1}$).

The position of a metal-hydrogen stretch in all transition metal hydrides typically shifts to higher energy upon descending a triad. This observation requires that metal-hydrogen bond strengths must be greater in the heavier metal congeners. This is evident in Entries 7-8 and 7-9 (Table I), where the $\nu(\text{MH})$ for TcH_9^{2-} is 50 cm^{-1} lower than for ReH_9^{2-} . The indication that TcH_9^{2-} has a weaker $\text{M}-\text{H}$ bond from IR analysis of $\nu(\text{MH})$ is also reflected in the greater reactivity (H/D exchange reactions) of TcH_9^{2-} over ReH_9^{2-} (57). It has been suggested that a polarization of a metal-hydrogen bond between $\text{M}^{\delta+}-\text{H}^{\delta-}$ is expected to lower the corresponding $\nu(\text{MH})$. Pez, Grey, and Corsi offer as example $\text{K}^+\text{Ru}(\text{H}_2)(\text{PPh}_3)_2\text{PPh}_2\text{C}_6\text{H}_4^-$ (Entry 8-18) which has a much lower $\nu(\text{MH})$ than the neutral ruthenium compounds, $[(\text{PPh}_3)_2\text{RuHCl}]_2$ or $(\text{PPh}_3)_3\text{Ru}(\text{N}_2)\text{H}_2$ (60).

Cation interactions have also been observed to affect the position of $\nu(\text{MH})$. For example, the $\nu(\text{MH})$ vibration in $\text{RuH}(\text{Me})(\text{PPh}_3)_2(\text{MeLiOEt}_2)_2$ is reportedly at 1610 cm^{-1} (83). It was proposed that a Li^+ interaction of the type $\text{Li}^+ \cdots \text{H}-\text{Ru}$ was responsible for the low frequency observed. This type of interaction lowers the $\nu(\text{MH})$ frequency either by polarizing the metal-hydrogen bond, as Pez, Grey, and Corsi have suggested, or by forming a pseudo-bridging hydride which has lower stretching frequencies than terminal metal hydrides. Cooper, Shriver, and Onaka have investigated the fundamen-

tal vibrations for bridging hydrides and have discussed the lower $\nu(\text{MH})$ (asymmetric, highest frequency mode, $\text{M}-\text{H} \rightarrow \text{M}'$) as arising from a weaker

three-center, two-electron bond ($\text{M} \begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \cdots \quad \cdots \end{array} \text{M}'$ or $\text{M} \cdots \text{H} \cdots \text{M}'$) compared to the stronger terminal two-center, two-electron bond (84). Strongly interacting metal cations with a hydride ligand may thus fall under this category. The $\text{M}-\text{H}$ bond stretching frequencies have also been shown to be very dependent on the $\text{M} \begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \quad \quad \end{array} \text{M}'$ interbond angle (85).

Carbonyl-containing compounds have the fewest reports of $\nu(\text{MH})$ bands. This may be due to overlapping $\nu(\text{CO})$ bands which are expected in the same region or to bands that are simply too weak and broad. Since $\nu(\text{CO})$ and $\nu(\text{MH})$ are close in energy, the two vibrations may couple into one another. This is easily measured by observing any shifts in $\nu(\text{CO})$ bands while isotopically exchanging hydrogen for deuterium. The greatest amount of coupling occurs in vibrational modes of the same symmetry and is most pronounced in the heavier metal congeners. This is easily seen in the $\text{HM}(\text{CO})_4^-$ series (Entries 8-1 through 8-6, Table I), where the symmetric A_1 modes are most greatly affected and osmium shows the largest shifts. It should be mentioned that the corresponding $\nu(\text{MD})$ vibrations, which are expected to be a factor of 1.4 to lower energy than $\nu(\text{MH})$ bands, are many times impossible to observe, as is the case in this example, due to interfering low frequency bands, especially from certain cations.

The $\nu(\text{CO})/\nu(\text{MH})$ coupling, in addition to being greatest among vibrations of the same symmetry, is largest when the groups are trans to one another. In a detailed vibrational analysis of $\text{HRe}(\text{CO})_5$ it was shown that $\nu(\text{CO})$ coupled into the $\nu(\text{MH})$ 400 times greater when the CO was in a trans position (86). There are examples, however, where coupling is not observable. In the group 6 hydrides, $\text{HM}(\text{CO})_5^-$ (Entries 6-1 to 6-5), H/D exchange showed small or nonexistent shifts in $\nu(\text{CO})$. In addition, neither the $\nu(\text{MH})$ nor $\nu(\text{MD})$ vibrations could be observed even with the aid of Raman spectroscopy (18a). The lack of observable metal—H/D bands and coupling to $\nu(\text{CO})$ is still a curious question.

The coupling of the $\nu(\text{MH})$ to $\nu(\text{CO})$ can be useful when the coupling is large. In these cases even though the $\nu(\text{MH})$ may be nonobservable, H/D exchange reactions can be effectively monitored by observing the $\nu(\text{CO})$ shifts.

B. Nuclear Magnetic Resonance

^1H NMR is especially diagnostic of anionic transition metal hydrides. The proton chemical shifts are seen at high fields, typically between -2 to

–15 ppm (Table I). The dinuclear metal hydrides have the highest shifts, presumably caused by the additional shielding provided by a second metal atom. The extraordinary high field chemical shifts observed for $\text{HRu}(\text{OEP})^-$ and $\text{HOs}(\text{OEP})^-$ ($\delta = -57.04$ and -66.06 ppm, respectively) are ascribed to effects of the octaethylporphyrin ring current (30).

The position of a metal hydride ^1H -NMR shift is difficult if not impossible to predict, and there are no clearcut trends that hold for all metal complexes. For example, anionic metal hydrides have field shifts no higher than neutral analogs. That is, $\text{HV}(\text{CO})_5^{2-}$, $\text{HCr}(\text{CO})_5^-$, and $\text{HMn}(\text{CO})_5$ are found at -4.76 , -6.73 , and -7.5 ppm, respectively; $\text{HFe}(\text{CO})_4^-$ and $\text{HCo}(\text{CO})_4$ are at -8.68 and -10.7 ppm, respectively (Table I). It is interesting to note that higher field shifts seem to accompany certain metals (such as Cr) regardless of the complex. This is exemplified for monomeric $\text{HM}(\text{CO})_5^-$ ($\text{M} = \text{Cr}$, -6.73 ppm; $\text{M} = \text{Mo}$ and W , ~ -4 ppm) as well as for dimeric $\mu\text{-HM}_2(\text{CO})_{10}^-$ ($\text{M} = \text{Cr}$, -19.5 ppm; $\text{M} = \text{Mo}$ and W , ~ -12.5 ppm). Group 6 heterobimetallic bridging hydrides show an average chemical shift indicating the high field influence of Cr ($\mu\text{-HCrW}(\text{CO})_{10}^-$, -15.4 ppm). The “chromium effect” is even observed in the mixed metal hydrides which contain a terminal iron hydride, $\text{HFeM}(\text{CO})_9^-$ ($\text{M} = \text{Cr}$, -13.4 ppm; $\text{M} = \text{W}$, -11.8 ppm) (Entries 8,6-1 and 8,6-2, Table I).

The well-proven method of tailoring the electronic character of low valent complexes by substituting CO with phosphorus donor ligands has been done for several hydrides (Category 2, Table I). In all cases the principal $\nu(\text{CO})$ shift is as expected for the donor character $\text{P}(\text{OR})_3 < \text{P}(\text{aryl})_3 < \text{P}(\text{alkyl})_3$, and the chemical reactivity of the MH^- functionality varies systematically as well (*vide infra*). Nevertheless the metal hydride chemical shifts show few obviously correlatable trends.

Phosphorus to hydrogen scalar coupling constants are of interest in P—ligand-substituted hydrides, especially in determining stereochemistry and dynamic behavior. For the known complexes, J_{PH} values generally vary $\text{TBP} < \text{Oh} < \text{SqPl}$, and may be naively rationalized on the basis of s orbital involvement in the two bond couplings, assuming the Fermi contact term for spin–spin coupling predominates. [*N.B.*: Information derived from changes in scalar coupling constants should be analyzed cautiously, bearing in mind that the *sign* of the coupling constant is in most cases not known.] As expected, phosphorus-to-proton coupling is larger when PR_3 is trans rather than cis to H in Oh or SqPl complexes. The *trans*- $\text{HFe}(\text{CO})_3\text{PR}_3^-$ series (Entries 8-7 through 8-12, Table I) show small J_{PH} values, rationalized because the communication between axial ligands in TBP structures is largely via a dp hybrid set, with smaller mixing of the equatorial sp^2 set. Interestingly, the J_{PH} in these latter anions is counterion, solvent, and temperature dependent (27). The interpretation of this phenomenon as of this writing is that subtle bond

angle changes alter the amount of *s* orbital mixed into the axial ligand-metal bonds (81).

C. Spectroscopic Studies of Ion Pairing

The $\nu(\text{CO})$ IR and ^1H -NMR techniques have been combined to elucidate site-specific contact ion pairing in salts of anionic carbonyl hydrides dissolved in low dielectric constant solvents (typically THF, $\epsilon = 7.6$). Table III lists data which show the extent of IR and NMR changes on replacement of large cations such as PPN^+ [earlier shown to be *associated* with the anions in THF solution, but not perturbing of their structures (87)] with a strongly interacting one such as Na^+ . The balance between the electrostatic potential of the cation and the competition of anion and solvent for interaction with the cation determines the extent of cation-anion interaction. For example, of the alkali cations, Na^+ usually shows the most extensive (by spectroscopy) ion pairing with anionic carbonyl hydrides in THF. The greater oxophilicity of Li^+ renders it highly solvated, and the large K^+ lacks the requisite electrostatic potential. Hence, Na^+ has the combination of qualities intermediate between Li^+ and K^+ to yield the greatest *number* of contact ion pairs.

The selection of a specific site on the anion for interaction by the cation is dependent on the charge polarization or sites of varying localized charge on the anion. The area of site-selective ion pairing in metal carbonylates has been reviewed (88), and there are detailed analyses of the same in hydrido metal carbonylates (27,80,89). Figure 5 summarizes much of this work. The carbonyl oxygen is the preferred interaction site in the hydrides $\text{HFe}(\text{CO})_4^-$, $\text{CpV}(\text{CO})_3\text{H}^-$, $\text{CpNb}(\text{CO})_3\text{H}^-$, and $\text{HCr}(\text{CO})_5^-$. The most prominent evidence for this is the asymmetric effect of added Na^+ on the $\nu(\text{CO})$ IR

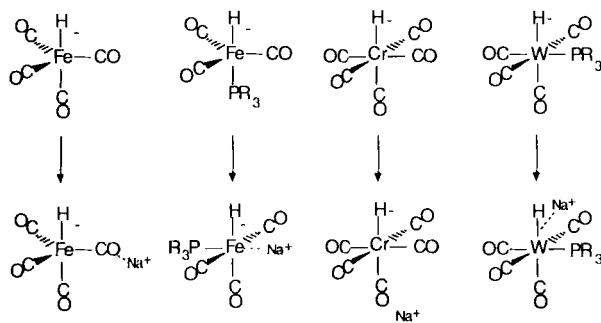


FIG. 5. Sites of Na^+ interaction with anionic metal carbonyl hydrides as established by $\nu(\text{CO})$ IR studies in THF solutions (27,80,89).

TABLE III
SPECTROSCOPY OF ION PAIRS OF SOME ANIONIC TRANSITION METAL HYDRIDES^a

Compound	δ (H ⁻) (ppm)	Solvent	Coupling constants, <i>J</i>	ν (CO) (cm ⁻¹)	Solvent	Reference
[PPN] CpV(CO) ₃ H	-6.72	THF		1890,1780	THF	14
Na CpV(CO) ₃ H				1890,1795,1780,1735	THF	14
[Et ₄ N] CpNb(CO) ₃ H	-5.6	MeCN	NbH = 36	1900,1789	MeCN	16
Na CpNb(CO) ₃ H				1897,1799,1739	THF	17
[PPN] HCr(CO) ₅	-6.73	THF		2017,1883,1852	THF	18
Li HCr(CO) ₅	-6.80	THF		2016,1885,1857	THF	89
Na HCr(CO) ₅	-6.75	THF		2016,1894,1884,1854,1814	THF	89
[PPN] HCr(CO) ₄ P(OMe) ₃	-7.00	THF	PH = 54	1971,1854,1817	THF	18
Na HCr(CO) ₄ P(OMe) ₃	-7.50	THF	PH = 52	1986,1865,1843	THF	89
[PPN] HW(CO) ₅	-4.10	THF	WH = 52.5	2029,1888,1856	THF	18
Li HW(CO) ₅	-4.35	THF		2030,1890,1860	THF	89
Na HW(CO) ₅	-4.40	THF		2030,1896,1890,1860,1822	THF	89
[PPN] HW(CO) ₄ PPh ₃	-3.0	MeCN	PH = 27	1974,1851,1815	THF	26
Li HW(CO) ₄ PPh ₃	-3.85	THF	PH = 26	2012,1894,1851	THF	89
Na HW(CO) ₄ PPh ₃	-3.70	THF	PH = 26	1987,1863,1826	THF	89
[PPN] HW(CO) ₄ PMe ₃	-3.6	MeCN	PH = 30, WH = 54	1969,1847sh,1842,1805	THF	26
Li HW(CO) ₄ PMe ₃	-5.05	THF	PH = 27	1985,1862,1824	THF	89
Na HW(CO) ₄ PMe ₃	-4.75	THF	PH = 28	1982,1858,1823	THF	89
[Et ₄ N] CpRe(CO) ₂ H	-12.35	MeCN		1846,1770	THF	21
K CpRe(CO) ₂ H	-12.38	MeCN		1859,1775,1760	THF	21

(continued)

TABLE III (continued)

Compound	δ (H^-) (ppm)	Solvent	Coupling constants, J	$\nu(CO)$ (cm^{-1})	Solvent	Reference
[PPN] $HFe(CO)_4$	-8.68	THF		1995,1905,1876	THF	80
Na $HFe(CO)_4$	-8.70	THF		2003,1910,1890,1854	THF	80
[PPN] $HFe(CO)_3P(OMe)_3$	-9.20	THF (22°C)	PH = 11.9	1941,1841	THF	27
[Et ₄ N] $HFe(CO)_3P(OMe)_3$	-9.33	THF (22°C)	PH = 8.99	1945,1850,1830	THF	27
Li $HFe(CO)_3P(OMe)_3$				1942,1842	THF	27
Na $HFe(CO)_3P(OMe)_3$	-9.28	THF (22°C)	PH = 11.2	1954,1942,1861, 1853,1841,1810	THF	27
[PPN] $HW_2(CO)_{10}$				2041,1940,1879	THF	41
[Et ₄ N] $HW_2(CO)_{10}$	-12.60	THF		2043,1943,1880	THF	38,41
Na $HW_2(CO)_{10}$	-12.58	THF	HC = 4.3, °3.5, WH = 42.1	2041,1941,1879	THF	31,38
[PPN] $HFe_2(CO)_8$				1987,1940,1880,1852,1770	THF	47
Na $HFe_2(CO)_8$	-8.47	THF (33°C)		1987,1940,1880 1852,1770,1730	THF	47
	-6.12	THF (-66°C)	CH = 5.5			47
[Na(cr)] $HFe_2(CO)_8$	-9.01	THF		1987,1940,1880,1852,1770	THF	47
Li $HFe_2(CO)_8$				1987,1940,1880, 1852,1770,1618	THF	47

^a Abbreviations used given in Table I.

spectrum. The $\nu(\text{CO})$ primarily associated with $\text{M}-\text{CO} \cdots \text{Na}^+$ will be moved to lower energies, whereas the loss of $d_\pi-\pi^*$ back-bonding will serve to raise the bond order and hence the stretching force constants of the other CO groups (Table III).

The sodium salt of $\text{HW}(\text{CO})_5^-$ apparently exists as an equilibrium of contact ion-paired forms with Na^+ interaction at the *trans*-CO oxygen as well as at the metal hydride site. Upon synthesizing the P-donor ligand derivatives, *cis*- $\text{HW}(\text{CO})_4\text{PR}_3^-$, both $\nu(\text{CO})$ IR and ^1H NMR indicated contact interaction solely at the $\text{W}-\text{H}$ site (89). That interaction is represented in Fig. 5 as simultaneous interaction of Na^+ with hydride and with W. The extent with which Na^+ interacts with W is not known. In fact, Fenske-Hall calculations (81) indicate the M in $\text{HM}(\text{CO})_5^-$ to bear a slight *positive* charge and the negative charge to be substantially on H and the CO groups. It is possible that the degree of $\text{Na} \cdots \text{W}$ interaction is indeed minimal. Certainly the X-ray structures presented earlier provide precedence for proposing $\mu\text{-H}(\text{Na}^+ \cdots \text{W}^-)$ interactions. The tungsten hydride interaction site is proposed on basis of the upfield ^1H shift for the Na^+ salt as compared to the PPN^+ salt, as well as the symmetrical effect of Na^+ on the $\nu(\text{CO})$ bands, i.e., they are all shifted to *higher* energies, indicating an electron drain somewhere in the anion.

As indicated in Fig. 5, the interaction site is an equatorial CO oxygen for $\text{Na}^+\text{HFe}(\text{CO})_4^-$ in THF. On substituting a CO group by PR_3 , we believe the evidence for $\text{Na}^+ \cdots \text{Fe}^-$ interaction is convincing (27). The $\nu(\text{CO})$ IR spectral patterns denote a change in symmetry (C_{3v} to C_s) as the counterion is changed from PPN^+ to Na^+ , and the $\nu(\text{CO})$ bands are shifted to higher energies. The particular structure proposed for $\text{Na}^+\text{HFe}(\text{CO})_3\text{PR}_3^-$, i.e., the Na^+ trans to PR_3 in the inner sphere contact interaction, is consistent with several points. Fenske-Hall molecular orbital calculations have shown negative charge to build up more on the Fe than on the H on replacing the axial CO of $\text{HFe}(\text{CO})_4^-$ with the representative donor ligand, PH_3 (81). It is also consistent with the mixed metal complexes $\text{HFeM}(\text{CO})_9^-$ and $\text{R}_3\text{P}(\text{OC})_3(\text{H})\text{FeM}(\text{CO})_5^-$ (Entries 8,6-2 and 8,6-3, Table I) discussed earlier, which demonstrate the tendency of TBP $\text{HFe}(\text{CO})_4^-$ and $\text{HFe}(\text{CO})_3\text{PR}_3^-$ to achieve $d^6\text{-Oh}$ status in the donor-acceptor complexes. The latter mixed metal complex has the PR_3 ligand trans to the $\text{Fe} \rightarrow \text{M}$ bond and cis to the $\text{Fe}-\text{H}$.

Finally, in the spirit of the last two paragraphs, it is then reasonable that the "donor-acceptor" complexes involving $\text{HM}(\text{CO})_5^-$ (M = group 6)

anions as in $\text{HM}_2(\text{CO})_{10}^-$, form that bond via the $\text{M} \begin{array}{c} \text{H}^- \\ \nearrow \quad \searrow \\ \text{M} \quad \text{M} \end{array}$ interaction, with little $\text{M} \cdots \text{M}$ interaction.

IV REACTIVITY

A. Scope of Reactions and Relative Reactivity

The scope of reactivity possible with anionic hydrides is illustrated in the reaction "clock," Fig. 6. The range of reactions shown have been demonstrated for the monomeric group 6 carbonyl hydrides, which have been extensively studied and in general exhibit quite clean reactions. Impressive selectivities have been noted in the area of organic functional group reductions (*vide infra*). Other active hydrides, e.g., $\text{CpV}(\text{CO})_3\text{H}^-$, undergo many of these reactions (14). Still other hydrides are reactive toward some substrates but not others. For example, whereas $\text{HM}(\text{CO})_5^-$ species ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) readily fix CO_2 (7 o'clock position, Fig. 6), the $\text{HFe}(\text{CO})_4^-$ anions are inert toward CO_2 , and the *trans*- $\text{HFe}(\text{CO})_3\text{PEt}_3^-$ shows reactivity, generating the formate ion, HCO_2^- (81). The $\text{HFe}(\text{CO})_4^-$ anion will, however, reduce $\alpha-\beta$

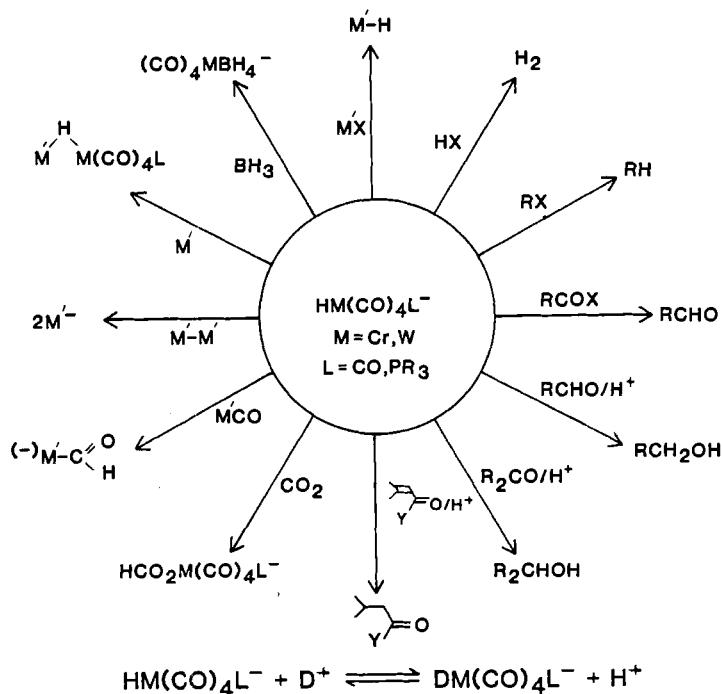
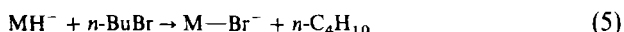


FIG. 6. Reactions of the Group 6 metal anionic carbonyl hydrides.

unsaturated ketones (6 o'clock, Fig. 6) in the presence of acid with considerable facility (47).

The extent to which a hydride is protonated (1 o'clock) or undergoes halide exchange with LiCl, for example (12 o'clock), clearly depends on "hydride character" or "hydricity." This concept, i.e., the ability of a transition metal to release hydrogen as H^- , is difficult to define experimentally because of the multiple pathways available for an overall H^- transfer. Nevertheless, a hydride reactivity scale modelled after the well-known and useful metal carbonyl anion nucleophilicity scale (90), has been established (5). Detailed kinetic studies have found the reduction of *n*-BuBr [Eq. (5)] to follow a second order rate expression [Eq. (6)]. The relative reactivity of a series of hydrides given in Fig. 7 is based on the ordering of second-order rate constants. Rate constants range from $0.050 \text{ second}^{-1} M^{-1}$ for *cis*-HW(CO)₄P(OMe)₃⁻ to $2.5 \times 10^{-4} \text{ second}^{-1} M^{-1}$ for *trans*-HFe(CO)₃P(OMe)₃⁻, and no reaction was observed at room temperature (RT) for HFe(CO)₄⁻ (5).



$$\text{rate} = k_2[\text{MH}^-][n\text{-BuBr}] \quad (6)$$

We have found the relative reactivity ordering given in Fig. 7 to be on the whole a satisfactory guide to reagent selection. Nevertheless, the hydride reactivity scale is somewhat substrate dependent. For example, reactivity of the more electron-rich hydrides *cis*-HM(CO)₄P(OMe)₃⁻ (M = Cr, W) with tertiary carbon centers as in *t*-BuBr, is diminished to a level less than HM(CO)₅⁻.

It should be noted that other hydrides mentioned in preceding sections of this article obviously have chemical reactivity. For example, a reactivity clock as impressive as Fig. 6 has been published for reactions of [Cp₂M(H)Li]₄ (M = Mo, W, structure 21) with primarily organic substrates (91). In many cases these reactions do not involve straightforward hydride transfer character [witness Eqs. (7) and (8), for example], and mechanistic or synthetic

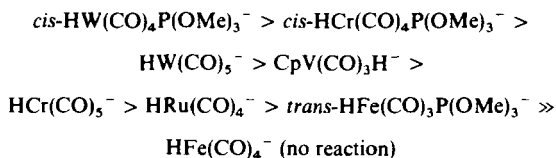
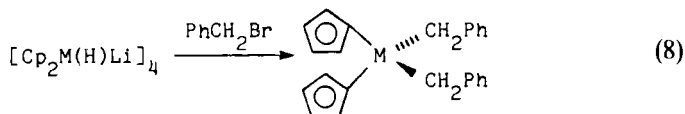
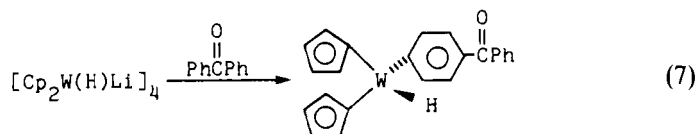


FIG. 7. Relative reactivity of anionic metal carbonyl hydrides based on second-order rate constants for reduction of *n*-C₄H₉Br to C₄H₁₀. Reprinted with permission from *Organometallics* 4, 83. Copyright (1985) American Chemical Society (5).

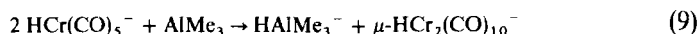
applications have not been explored. Despite the exciting nature of such reactions, their incomplete state suggests we omit them at this time.



B. Reactions of Anionic Hydrides with Electrophiles

1. Main Group Lewis Acids

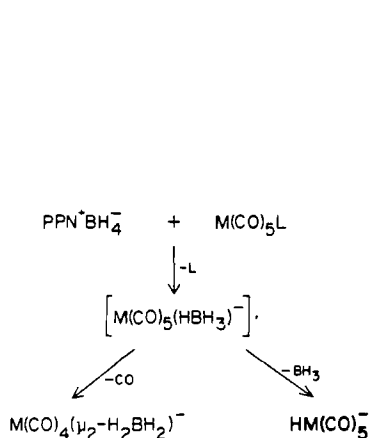
The negative character of the anionic hydrides is further exemplified in reactions with Lewis acids. Trimethylaluminium reacts with $\text{HCr}(\text{CO})_5^-$ according to Eq. (9) (18b). Interestingly, all the $\text{Cr}(\text{CO})_5^0$ produced by hydride



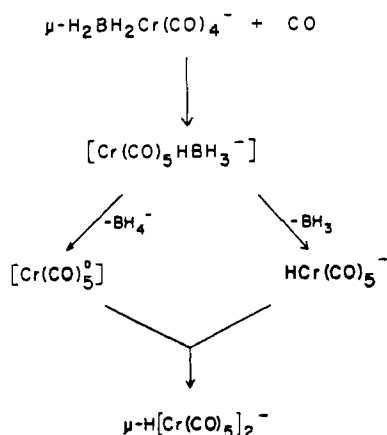
abstraction is quantitatively scavenged by reactant $\text{HCr}(\text{CO})_5^-$, even in the presence of excess AlMe_3 . The $\text{HCr}(\text{CO})_5^-$ ligates $\text{Cr}(\text{CO})_5^0$ preferentially to AlMe_3 , generating the $\mu\text{-HCr}_2(\text{CO})_{10}^-$ anion which is stable to hydride abstraction.

A reaction similar to Eq. (9) occurs with $\text{BH}_3 \cdot \text{THF}$ as acid at 0°C , forming $\mu\text{-HCr}_2(\text{CO})_{10}^-$ quantitatively. At 22°C , however, a mixture of $\mu\text{-HCr}_2(\text{CO})_{10}^-$ and $\text{H}_2\text{B}(\mu\text{-H})_2\text{Cr}(\text{CO})_4^-$ [Eq. (2)] is formed. The higher temperature is required for $\text{Cr}-\text{CO}$ bond breaking. In fact, there are $\nu(\text{CO})$ IR bands observed during the course of this reaction that imply the intermediacy of the monodentate borohydride, $(\text{OC})_5\text{Cr}(\mu\text{-H})\text{BH}_3^-$. Similar bands also arise during the course of reaction of BH_4^- with a labile ligand precursor to $\text{M}(\text{CO})_5^0$, e.g., (piperidine) $\text{M}(\text{CO})_5$. As indicated in Schemes 4 and 5, the loss of CO from the intermediate is reversible. Isolated $\text{Cr}(\text{CO})_4(\mu\text{-H})_2\text{BH}_2^-$ reacts with CO to yield $\text{HCr}(\text{CO})_5^-$, $\mu\text{-HCr}_2(\text{CO})_{10}^-$, BH_4^- , and (presumably) $\text{OC} \rightarrow \text{BH}_3$.

Hence, the Lewis acidity of low valent transition metal carbonyls toward anionic hydrides would seem to be comparable to that of group 3 Lewis acids.



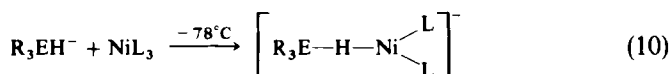
SCHEME 4. Reprinted with permission from *J. Am. Chem. Soc.* **104**, 6961. Copyright (1982) American Chemical Society (18a).



SCHEME 5. Reprinted with permission from *J. Am. Chem. Soc.* **104**, 6961. Copyright (1982) American Chemical Society (18a).

Similar strong interactions are observed for neutral hydrides; the interesting $\text{Cp}_2\text{W(H)}_2\cdot\text{AlMe}_3$ structure indicates adduct formation via two $\text{W}(\mu\text{-H})\text{Al}$ bridges (92). A strong adduct between Cp_2TaH_3 and AlMe_3 is known (93).

Hydride anions analogous to the proposed monodentate borohydride complexes have been observed in the case of R_3EH^- ($\text{E} = \text{Al, Ga}$) adducts of Ni^0 derivatives [Eq. (10)] (24). Such mixed metal hydrides are thermally sensitive, decomposing at temperatures above -50°C . The acceptor strength



of the nickel complex varies $\text{Ni(CDT)} < \text{Ni(C}_2\text{H}_4)_2 < \text{Ni(CO)}_3$. In fact, when CO is passed through a solution containing $\text{Na}^+(\text{THF})_x[\text{i-Bu}_3\text{Al-H-Ni(C}_2\text{H}_4)_2]^-$, both C_2H_4 ligands are displaced, as well as the Bu_3Al acid, yielding $\text{Na(THF)}_x^+\text{HNi(CO)}_3^-$ (24). The pronounced tendency for the hydride to bridge two transition metals is again observed in this class of anions. Upon addition of TMEDA to the monomer, reaction (11) occurs. The

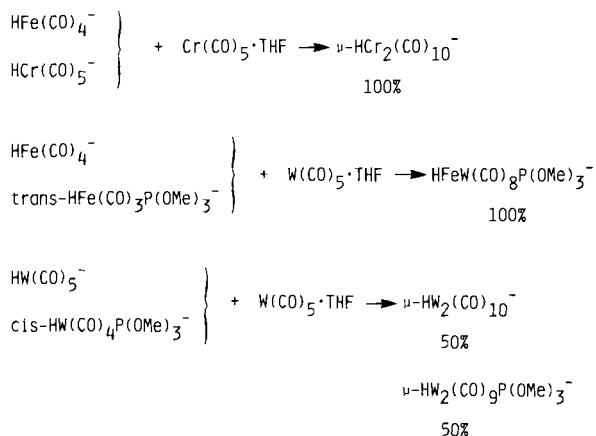


NaH was not clearly identified; it is expected based on reaction mass balance and earlier precedents (89,94,95).

2. Lewis Acids: Transition Metal Acceptors

The ability of anionic transition metal hydrides to serve as donor ligands to transition metal acceptors is well known, and the approach has been used in the designed synthesis of interesting mixed metal complexes (96,97). It is also important in terms of establishing a reaction mechanism when a traditional ligand such as PPh_3 is used as a scavenger for coordinatively unsaturated organometallics in the presence of anionic hydrides (14). Scheme 6 has examples of the approach used to establish *relative* competitive displacement of THF from $\text{THF} \cdot \text{M}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{W}$) by several anionic hydrides, a metal carbonylate anion, and some traditional ligands. The results of the study imply the following (98):

1. Negatively charged ligands are kinetically more competitive than neutral analogs.
2. Replacement of CO by a better donor ligand enhances kinetic (and thermodynamic) ligating ability in the case of $\text{HFe}(\text{CO})_4^-$ versus *trans*- $\text{HFe}(\text{CO})_3\text{P}(\text{OMe})_3^-$.
3. Replacement of CO by $\text{P}(\text{OMe})_3$ in the group 6 hydrides, $\text{HW}(\text{CO})_5^-$ versus *cis*- $\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3^-$, however, does not enhance kinetic (or thermodynamic) ligating ability, presumably due to steric encumbrance at the reactive $\text{W}-\text{H}$ site and also to steric encumbrance in the product, $\mu\text{-HW}_2(\text{CO})_9\text{P}(\text{OMe})_3^-$. The $\text{P}(\text{OMe})_3$ ligand in the dimer is *cis* to the



SCHEME 6. Competitive ligation of $\text{M}(\text{CO})_5 \cdot \text{THF}$ by anionic transition metal hydrides in THF solution. Kinetic ligation order: *cis*- $\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3^- \sim \text{HW}(\text{CO})_5^- > \text{HCr}(\text{CO})_5^- \sim \text{Br}^- > \text{trans-HFe}(\text{CO})_3\text{P}(\text{OMe})_3^- > \text{Mn}(\text{CO})_5^- > \text{HFe}(\text{CO})_4^- > \text{PPh}_3$.

hydride bridge and experiences steric repulsion from the CO groups on the adjacent $\text{W}(\text{CO})_5$ unit.

4. Structural rearrangement appears to inhibit ligation ability: $\text{HM}(\text{CO})_5^- > \text{HFe}(\text{CO})_4^-$, and $\text{HM}(\text{CO})_5^- > \text{Mn}(\text{CO})_5^-$. Nevertheless, when structural reorganization must occur (as in $\text{TBP} \rightarrow \text{Oh}$) the hydride has no apparent advantage over the metal carbonylate: $\text{Mn}(\text{CO})_5^- > \text{HFe}(\text{CO})_4^-$.

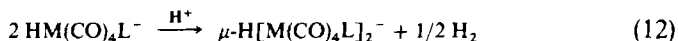
3. Brønsted Acids

The protonation of anionic transition metal hydrides is an important step in the production of H_2 via the water–gas shift reaction (Scheme 1) as well as in the production of neutral hydrides which are apparently more apt than anionic hydrides to undergo hydrogen transfer (insertion reactions) to nonpolar substrates such as olefins (99). In addition, it is important to establish the stability of hydrides toward acids because the “useful hydride transfer chemistry” implicated in Scheme 1 will frequently need to be carried out in the presence of H^+ (e.g., the stepwise H^-/H^+ , reduction of aldehydes and ketones, *vide infra*).

One might attempt to correlate the reactivity of anionic metal hydrides with the thermodynamic acidity of their conjugate acids. For example, Norton and co-workers find the $\text{p}K_a$ values of $\text{H}_2\text{M}(\text{CO})_4$ (determined in CH_3CN) to vary $\text{Fe} (11.4) < \text{Ru} (18.7) < \text{Os} (20.8)$ (99). Thus the weaker conjugate base for the pair $\text{HFe}(\text{CO})_4^- < \text{HRu}(\text{CO})_4^-$ we have found to be the weaker nucleophile in the RX reductions. Unfortunately the known $\text{p}K_a$ values of metal hydrides are very limited. The conjugate acids of the $\text{HM}(\text{CO})_5^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and $\text{CpV}(\text{CO})_3\text{H}^-$ hydrides are not isolable. In fact it is almost certain that protonation of the group 6 hydrides results in the formation of highly unstable $\eta^2\text{-H}_2$ complexes rather than the oxidative addition dihydride products analogous to $\text{H}_2\text{Fe}(\text{CO})_4$ and $\text{H}_2\text{Ru}(\text{CO})_4$. On the other hand, reactions of anionic hydrides with Brønsted acids indicate that the $\text{HM}(\text{CO})_5^-$ hydrides are protonated by far weaker acids than is the $\text{HFe}(\text{CO})_4^-$ hydride (*vide infra*). Hence at this point we conclude that base strengths and nucleophilicities of the MH^- anions most likely correlate well, regardless of the mode of bonding of the hydrogen (or the site of protonation).

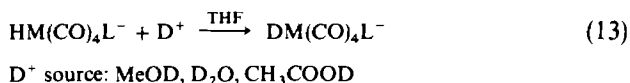
As indicated above, the relative reactivity of the anionic hydrides with protonic acids parallels their relative reactivity as given in Fig. 7. For example, $\text{HFe}(\text{CO})_4^-$ is stable to water, $\text{HCr}(\text{CO})_5^-$ reacts slowly (~ 1 hour) with 10 equivalents of water in THF at 22°C , and *cis*- $\text{HW}(\text{CO})_4\text{PMe}_3^-$ is extremely reactive to even trace amounts. For the group 6 hydrides the reaction is given by Eq. (12) (18). Also, as expected, the decomposition rate to produce H_2

depends on the acidity. The reaction described by Eq. (12) was monitored using a 100-fold excess of acid to $\text{HW}(\text{CO})_5^-$ in THF. The observed reaction



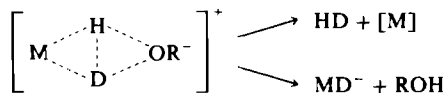
rates diminished as acid strengths diminished: $\text{HBF}_4 > \text{CH}_3\text{COOH} > \text{PhOH} > \text{H}_2\text{O} > \text{CH}_3\text{OH}$. Reaction rates were also faster in the more polar solvent, CH_3CN .

The moderate stability of these anionic hydrides to low concentrations of acids in THF solution was used to the following advantage. Gaus *et al.* (18*d*) were able to observe H/D exchange reactions using the deuterium sources indicated in Eq. (13).



Dependent on the hydridic character of the anionic hydride, a D⁺ source could be chosen so as to maximize the exchange rate and minimize the decomposition rate [Eq. (12)]. For example, MeOD is the reagent of choice for $\text{HW}(\text{CO})_4\text{PMe}_3^-$; however, $\text{HFe}(\text{CO})_4^-$ does not exchange with CH_3OD . In fact H/D exchange with D₂O is slow for $\text{HFe}(\text{CO})_4^-$, and CH₃COOD is the reagent of choice for this less active hydride.

The proposed exchange mechanism for H/D exchange in $\text{HM}(\text{CO})_5^-$ anions was that of a multi-centered transition state, or an OR^- [R = H, Me, or C(O)Me] stabilized dihydride. As the base strength of OR^- is diminished or as its leaving ability is enhanced by polar solvents, HD elimination [Eq. (12)] becomes competitive with H/D exchange. Interestingly, the proposed transition state changes into an $\eta^2\text{-H}_2$ complex, known for group 6 metals, when the elimination of H₂ (or HD) is the pathway followed.



4. Small Molecule Electrophiles

The 7 o'clock position of the reactivity wheel (Fig. 6) shows reactions of anionic hydrides with CO₂. This area was recently reviewed (100) and will not be discussed here except to say that the order of reactivity toward CO₂ is the same as the RX reactivity (Fig. 7). Sulfur dioxide readily removes H⁻ from more active hydrides. Carbon monoxide does not appear to react with the hydrides unless activated by a metal. For example the presence of $\text{Fe}(\text{CO})_4\text{CHO}^-$ in the products of reaction of $\text{HW}(\text{CO})_5^-$ or $\text{CpV}(\text{CO})_3\text{H}^-$ with $\text{Fe}(\text{CO})_5$ is believed to be due to hydride transfer to coordinated CO.

C. Reactions of Anionic Hydrides with Organic Substrates

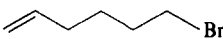

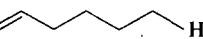
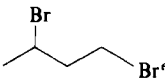
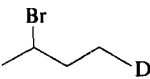
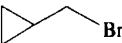

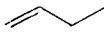
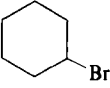
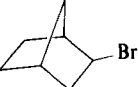
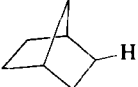
Anionic transition metal hydrides have been used as formal hydride transfer reagents for a variety of organic substrates. These reactions are similar in form to the main group element reductants, NaBH_4 , LiAlH_4 , and derivatives. Reductions by main group element hydrides and transition metal hydrides are also related in the complexity of mechanism(s) whereby the H^- is transferred, i.e., two-electron, H^- transfer or some radical process. This section describes studies of stoichiometric reductions of alkyl halides, acid chlorides, aldehydes, and ketones by transition metal hydrides. Although impressive selectivities and stereospecificities are evident in some reactions, synthetic difficulties and air sensitivity limit synthetic usefulness at the current stage of development. However, since anionic transition metal hydrides are regenerable from inexpensive starting materials, CO and base (Scheme 1), fundamental knowledge of their reaction chemistry should encourage technical developments in hydride synthesis.

1. Alkyl Halides

Hydride reduction of alkyl halides by anionic transition metal hydrides has been investigated extensively in only a few cases: $\text{HM}(\text{CO})_4\text{L}^-$ [M = group 6; L = CO , PR_3 , $\text{P}(\text{OR})_3$], $\text{CpV}(\text{CO})_3\text{H}^-$, and $\text{HFe}(\text{CO})_4^-$ (5,14c,101). Table IV gives examples of these reductions and yields. Note that the H/D exchange reaction described above can be used *in situ* to deliver D selectively to the primary carbon center in 1,3-dibromobutane. Alkyl coupling products have not been observed as products of these reactions, and elimination products are rarely seen (5). The organometallic products are in the cases of $\text{HM}(\text{CO})_4\text{L}^-$ (M = Cr, W; L = CO , PR_3) and $\text{CpV}(\text{CO})_5\text{H}^-$ the simple H^-/X^- exchange product. In a few reactions of the latter reductant, the $\mu\text{-H}[\text{CpV}(\text{CO})_3]_2^-$ product is seen (14). The dimeric hydride is believed not to be a primary product but rather results from $\text{CpV}(\text{CO})_3\text{H}^-$ displacement of X^- from the $\text{CpV}(\text{CO})_3\text{X}^-$ primary product. The fact that $\mu\text{-HM}_2(\text{CO})_{10}^-$ is not seen in any of the group 6 reductions suggests free $\text{M}(\text{CO})_5^0$ is not produced, for it is known to rapidly and quantitatively aggregate with the starting material, $\text{HM}(\text{CO})_5^-$, at the same rate as Br^- .

Both the group 6 carbonyl hydrides and $\text{CpV}(\text{CO})_3\text{H}^-$ show second-order kinetics with alkyl halides [Eq. (6)]. The dependence of reactivity on X was $\text{I} > \text{Br} > \text{Cl}$. Alkyl tosylates, reagents not expected to react via SET processes, reacted with $\text{HM}(\text{CO})_4\text{P}(\text{OMe})_3^-$ (M = Cr, W) with rates similar to the corresponding alkyl bromides; however, $\text{CpV}(\text{CO})_3\text{H}^-$ and $\text{HCr}(\text{CO})_5^-$ were quite inert with alkyl tosylates. The $\text{HW}(\text{CO})_5^-$ anion reduced alkyl tosylates slowly.

TABLE IV
 PRODUCTS OF REACTION OF METAL HYDRIDES^a WITH ORGANIC HALIDES

Halide	Product	HW(CO) ₅ ⁻ (5) yield (%) ^b	CpV(CO) ₃ H ⁻ (14c) yield (%) ^b
<i>n</i> -C ₄ H ₉ Br	<i>n</i> -C ₄ H ₁₀	83	—
2-C ₄ H ₉ Br	<i>n</i> -C ₄ H ₁₀	85	—
<i>t</i> -C ₄ H ₉ Br	<i>i</i> -C ₄ H ₁₀	81	100
<i>n</i> -C ₄ H ₉ I	<i>n</i> -C ₄ H ₁₀	89	—
<i>n</i> -C ₄ H ₉ Cl	NR	NR	NR
C ₆ H ₅ CH ₂ Cl	C ₆ H ₅ CH ₃	85	—
C ₆ H ₅ CH ₂ Br	C ₆ H ₅ CH ₃	99	90
C ₆ H ₅ COCl	C ₆ H ₅ CHO	80	40
C ₆ H ₅ CH(CH ₃)Br ^c	C ₆ H ₅ CH(CH ₃)D	95	64
α -Bromocamphor ^d	Camphor	70	—
C ₆ H ₅ Br	C ₆ H ₆	80	43
1-Bromoadamantane	Adamantane	70	60
	 +  H	80	85
		90	—
	 + 	80	—
	<i>c</i> -C ₆ H ₁₂	> 80	65
	 H	> 80	—

^a Metal hydrides as PPN⁺ salts. NR, No reaction.^b Gas chromatography yields.^c Isolated DW(CO)₅⁻ used.^d Isolated yield.^e DW(CO)₅⁻ generated *in situ*.

The data of Table V compare the reactivities of several metal hydrides toward *n*-C₄H₉Br, 2-C₄H₉Br, and *t*-C₄H₉Br. With *n*-BuBr reactivity differences between the simple anionic carbonyl hydrides could be established, presumably free from steric influences. The first column in Table V indicates greater reactivity for the heavier congener of an isostructural anion (W > Cr; Ru ≫ Fe), as well as for phosphite-substituted anions as com-

TABLE V
REACTION OF PPN^+HM^- WITH RX : DEPENDENCE ON PPN^+HM^- ^a
Rate = $k_2[\text{HM}^-][\text{RX}]$

M	$k_2 \times 10^3 \text{ second}^{-1} M^{-1}$ ^b		
	<i>n</i> -C ₄ H ₉ Br	2-C ₄ H ₉ Br	<i>t</i> -C ₄ H ₉ Br
Cr(CO) ₅	1.79 (±0.05)	1.65 (±0.28)	3.17 (±0.08)
W(CO) ₅	3.31 (±0.13)	1.79 (±0.05)	2.81 (±0.16)
Cr(CO) ₄ P(OCH ₃) ₃	30	1.89 (±0.06)	0.81 (±0.05)
W(CO) ₄ P(OCH ₃) ₃	50	4.24 (±0.18)	0.21 (±0.01)
CpV(CO) ₃	2.20 (±0.06)	—	0.33 (±0.03)
Ru(CO) ₄	1.0 ^c	—	—
Fe(CO) ₄	NR ^d	NR ^d	NR ^d
Fe(CO) ₃ P(OCH ₃) ₃	0.25 (±0.002) ^e	—	—

^a Reprinted with permission from *Organometallics* **4**, 83. Copyright (1985) American Chemical Society (5).

^b Error limits represent 90% confidence limit. Reactions were carried out at 26°C.

^c This system was not well behaved; value of k_2 estimated from half-life.

^d NR, No reaction.

^e Determined in the presence of a 10-fold excess of P(OMe)₃.

pared to all-CO analogs. The relative reactivity implied by these rate constants for $\text{CpV}(\text{CO})_3\text{H}^-$ and $\text{HW}(\text{CO})_5^-$ was substantiated by a competition study in which a deficiency of *n*-BuBr was added to an equimolar mixture of the two hydrides. The less reactive $\text{CpV}(\text{CO})_3\text{H}^-$ survived the reaction; all $\text{HW}(\text{CO})_5^-$ was converted to $\text{BrW}(\text{CO})_5^-$.

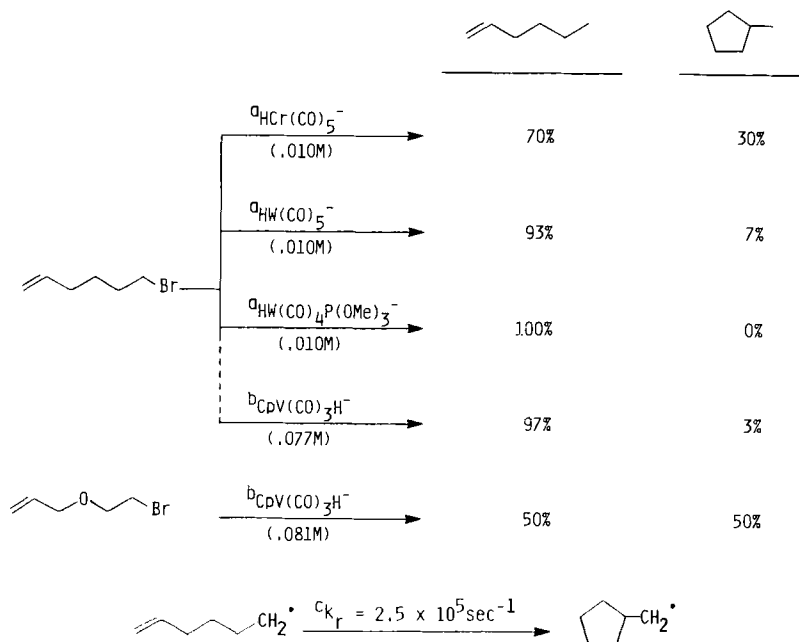
Although $\text{HFe}(\text{CO})_4^-$ reacts with MeI, there was no reaction of $\text{HFe}(\text{CO})_4^-$ with C₄ aliphatic alkyl bromides, cyclohexyl bromide, or *n*-octyl bromide at room temperature. Reaction of $\text{HFe}(\text{CO})_4^-$ with benzyl chloride occurred extremely slowly (days). The reduction of C₆H₅C(O)Cl, with $\text{Me}_4\text{N}^+\text{HFe}(\text{CO})_4^-$ (2:3 molar ratio) in CH₂Cl₂ solvent, is reported to require 1.25 hours (yielding benzaldehyde, 91%) (102). For comparison $\text{PPN}^+\text{HW}(\text{CO})_5^-$ was reacted with the same acid chloride in a 1:1 ratio in THF. The reaction was complete within minutes, and benzaldehyde was obtained as sole organic product (5); $\text{ClW}(\text{CO})_5^-$ was the organometallic product.

As discussed above for $\text{HW}(\text{CO})_5^-$, the $\text{HCr}(\text{CO})_5^-$ anion reacts with almost equal facility with the primary, secondary, and tertiary butyl bromides, and there are only minor differences between the reactivity of $\text{HCr}(\text{CO})_5^-$ and $\text{HW}(\text{CO})_5^-$. The P(OMe)₃-substituted group 6 hydrides are, however, about two orders of magnitude more reactive with *n*-BuBr than are their all-CO analogs. The data in the second column of Table V, reactivity with

2-C₄H₉Br, show less of a difference between the P(OMe)₃-substituted and the unsubstituted 6B metal hydrides. For example, *cis*-HW(CO)₄P(OMe)₃⁻ is only one order of magnitude more reactive than HW(CO)₅⁻, and both chromium hydrides are of similar reactivity. This trend develops further in the last series of Table V. With the highly hindered *t*-C₄H₉Br, the P(OMe)₃ derivatives are actually *less* reactive than HW(CO)₅⁻ or HCr(CO)₅⁻. Again the difference is most pronounced for the tungsten hydrides.

2. Mechanism of the Halide Displacement Reaction

A variety of observations and mechanistic probes, including the popular "radical clock substrate," have been used to aid the understanding of hydride transfer pathways. The radical probe reagent shown in Scheme 7 utilizes the skeletal rearrangement of the hexenyl radical as an indication of the existence of single electron transfer pathways. The important caveat to the utility of these reagents is that the rate of hydrogen atom abstraction from the 1-hexenyl radical must be slower than the skeletal rearrangement, else S_N2 and SET products are indistinguishable. For example, Scheme 7 shows the ratio of



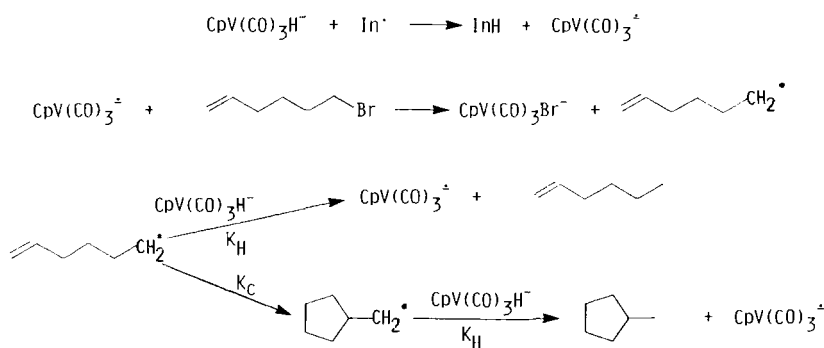
SCHEME 7. Notes: ^aRadical probe used in a sixfold excess (81). ^bMetal hydride used in a fourfold excess (14). The analogous oxy product is obtained with 2-allyloxyethyl bromide. ^cFrom Ref. 103.

uncyclized to cyclized product to be of the order of 97:3 for $\text{CpV}(\text{CO})_3\text{H}^-$ reaction. It was observed that this ratio increased linearly with increasing $\text{CpV}(\text{CO})_3\text{H}^-$ concentration. Furthermore, results from the product distribution of the ether analog of hexenyl bromide (Scheme 7), expected to have a faster cyclization rate than 1-hexenylbromide, supported the contention of Kinny, Jones, and Bergman that the low yield of cyclized product in the hexenylbromide probe resulted from a fast rate of hydrogen transfer (14c). The following radical chain process was proposed (Scheme 8). The hydrogen atom source was established to be $\text{CpV}(\text{CO})_3\text{H}^-$, and the chain continues when $\text{CpV}(\text{CO})_3^-$ abstracts $\text{Br}\cdot$ from 1-hexenyl bromide. The apparent hydrogen atom transfer rate, k_{H} , was estimated to be $2 \times 10^7 \text{ second}^{-1} \text{ M}^{-1}$ for *n*-alkyl radicals (14).

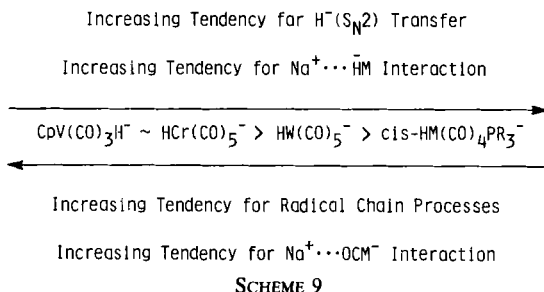
Further proof of the one-electron reduction mechanism for reactions of $\text{CpV}(\text{CO})_3\text{H}^-$ with alkyl halides is as follows (14c): *gem*-Dihalocyclopropanes reacted to replace only one halogen atom with a reasonable rate. This behavior is reminiscent of that observed in trialkyltin hydride reductions. When 1,2-dibromoalkenes were used, debromination occurred in contrast to reduction. Stereochemical reactions were carried out using optically active carbon centers, and only racemic products could be obtained (14c).

Scheme 7 also indicates reactions of other anionic hydrides with hexenylbromide. Clearly the results from the *cis*- $\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3^-$ anion are quite different from the other hydrides. In addition, the *cis*- $\text{HM}(\text{CO})_4\text{P}(\text{OMe})_3^-$ reagents showed almost total selectivity for primary carbon centers in competition experiments. Reduction rates of alkyl tosylates with $\text{HM}(\text{CO})_4\text{L}^-$ were also of the same order as corresponding alkyl bromides. Ion pairing studies of $\text{HM}(\text{CO})_4\text{L}^-$ complexes showed the greatest amount of direct cation interaction with the hydride ligand (89). All of this evidence supports

a direct two-electron hydride attack on organic substrates; i.e., $\text{M}-\text{H} \rightarrow \text{RX}$.



SCHEME 8



In contrast to the $HM(CO)_4L^-$ compounds, $HW(CO)_5^-$ and $HCr(CO)_5^-$ appeared to have substantial radical reduction behavior. Reduction of organic tosylates was *very* slow with $HW(CO)_5^-$ and almost inert with $HCr(CO)_5^-$, in contrast to rapid reduction rates with alkyl bromides. Radical probe reactions with these reductants also gave large amounts of rearranged products. Consistent with radical behavior in these reactions, selectivity for primary carbon centers was very low (Table V). Competition experiments for primary centers using $n\text{-C}_4\text{H}_9\text{Br}/t\text{-C}_4\text{H}_9\text{Br}$ mixtures yielded products $n\text{-C}_4\text{H}_{10}/t\text{-C}_4\text{H}_{10}$ in ratios of 75/25 for $HW(CO)_5^-$ and 15/85 for $HCr(CO)_5^-$, in contrast to $HW(CO)_4P(OMe)_3^-$ which gave only traces of reduction at the tertiary carbon center.

Information gleaned from the Kinney, Bergman, and Jones studies (14) combined with that from the Kao *et al.* study (5) suggests an increasing tendency for hydrides to follow a S_N2 or H^- transfer character in their reactions with RBr as indicated in Scheme 9. This order correlates well with the ability of Na^+ to interact with the anion at the $M-H^-$ bond site. A delocalization of negative charge, as indicated by Na^+ interaction with carbonyl oxygen, seems to correlate with increased radical behavior in reduction reactions. Since ion pairing studies are the most direct measure of fundamental differences in electron density distribution in these anions, a correlation is to be expected regardless of mechanism.

At this point we note that the *trans*- $HFe(CO)_3PR_3^-$ anions also reduce RBr to alkanes (5), albeit more slowly than the hydrides mentioned above. We have proposed that these reductions proceed via an oxidative addition pathway [Eq. (14)], based on the following observations:



1. $HFe(CO)_3P^-$ anions are selective for primary carbon centers; those hydrides with the most radicallike behavior are nonselective or [as in $HCr(CO)_5^-$] are, in fact, selective for tertiary centers.

2. No cyclized products result from the 1-hexenylbromide reductions. [Again, the caveat of k_H (trapping) versus k (rearrangement) applies.] Nevertheless those hydrides with radicallike behavior show some rearranged products..
3. Ion pairing studies (27) indicate inner sphere contact ion pairs are formed with direct $\text{Na}^+ \cdots \text{Fe}^-$ interaction.
4. The class of mixed metal anions, $\text{HFeM}(\text{CO})_9^-$, show the $\text{M}(\text{CO})_5^0$ electrophile interacting at the Fe center (48).

The last two points are accepted as clear indications of the considerable negative charge (or availability of the HOMO) at the Fe center in such anions. If such well-defined electrophiles as Na^+ or $\text{W}(\text{CO})_5^0$ add to the $\text{Fe}^{\delta-}$ center, then alkyl halides should also. As indicated before, such interactions lead the Fe^0 in a d^8 , TBP configuration, to a quasi- Fe^{II} , d^6 , Oh configuration, i.e., there are high lying nonbonding electrons that render the Fe center nucleophilic.

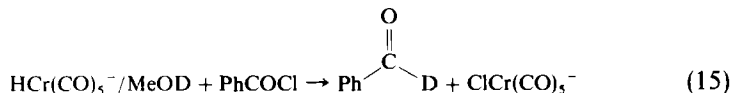
To summarize, we propose that *three* pathways are operative for alkyl halide reductions by anionic transition metal hydrides: (1) $\text{S}_{\text{N}}2$, hydride site nucleophilicity [$\text{HW}(\text{CO})_4\text{PR}_3^-$]; (2) radical chain pathways [$\text{CpV}(\text{CO})_3\text{H}^-$, $\text{HCr}(\text{CO})_5^-$]; and (3) $\text{S}_{\text{N}}2$, metal site nucleophilicity [$\text{HFe}(\text{CO})_3\text{PR}_3^-$]. The $\text{HW}(\text{CO})_5^-$ anion apparently reacts via a combination of $\text{S}_{\text{N}}2$ and radical chain pathways. In fact, a very recent study, which analyzed rates from a hindered skeletal rearrangement probe (not susceptible to $\text{S}_{\text{N}}2$ attack) and a nonhindered probe (1-hexenylbromide), concluded that both $\text{HCr}(\text{CO})_5^-$ as well as $\text{HW}(\text{CO})_5^-$ exercise considerable $\text{S}_{\text{N}}2$ and less radical chain [10% for $\text{HCr}(\text{CO})_5^-$ and 0.3% for $\text{HW}(\text{CO})_5^-$] character in reactions with 1-hexenylbromide (103a). Interestingly, in all cases where $\text{M}-\text{CO}$ or $\text{M}-\text{PR}_3$ bond lability is not problematical, good to excellent kinetic data are obtained and the second-order rate law obtains.

It must be noted that the conclusions expressed above regarding pathway are established for RBr only. The path is expected to be substrate dependent. For example, there is no indication that reductions of acyl halides by any of the $\text{M}-\text{H}^-$ anions proceed by a radical chain pathway. Stronger electrophiles are expected to promote ionic (H^- transfer) pathways.

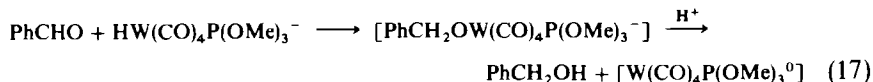
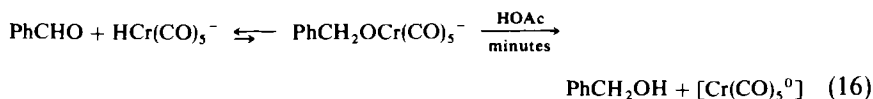
3. Acid Halides, Aldehydes, and Ketones

Reaction of all anionic hydrides described above with acyl halides leads to hydrogen/halogen exchange, yielding the corresponding aldehydes. Reaction of $\text{CpV}(\text{CO})_3\text{H}^-$ with $\text{C}_6\text{H}_{13}\text{COCl}$, PhCOCl , and PhCH_2COCl instantaneously yielded the corresponding aldehydes, $\text{C}_6\text{H}_{13}\text{CHO}$ (100%, gas chromatography), PhCHO (40%, isolated), and PhCH_2CHO (87%), with no observed alcohol products (14). The $\text{HFe}(\text{CO})_4^-$ anion requires longer times and a 2:3 molar ratio [the $\text{HFe}_3(\text{CO})_{11}^-$ anion is a product (102)];

nevertheless, the ease of synthesis and handling of $\text{HFe}(\text{CO})_4^-$ makes it an attractive reagent. The group 6 anionic hydrides also give high yields of aldehydes from a wide variety of acid halides (104). When the H/D exchange reaction [Eq. (13)] was coupled to acyl halide reduction, a deuterated aldehyde was obtained [Eq. (15)].

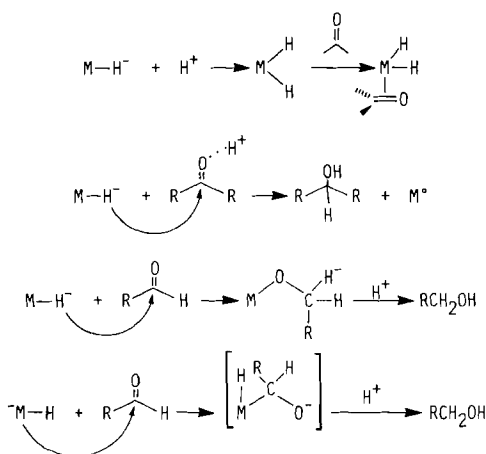


Overreduction of the aldehyde product does not occur with the weaker hydride donors such as $\text{CpV}(\text{CO})_3\text{H}^-$ or $\text{HCr}(\text{CO})_5^-$. In fact, NMR spectra showed excess $\text{HCr}(\text{CO})_5^-$ to coexist with the PhCHO product over long periods of time. *Only* when an equivalent of acetic acid was added was the aldehyde converted to alcohol, rapidly and quantitatively [Eq. (16)]. In contrast, the more active hydrides, *cis*- $\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3^-$, reacted with PhCHO to yield a spectroscopically observable intermediate, presumed to be the aldehyde addition product as indicated in Eq. (17) (105).



The group 6 anionic hydrides also reduce ketones, but only in the presence of acids (105). No intermediate alkoxides were ever observed. Studies of the acid dependence of these reactions suggest that an optimum pK_a exists for the required acid. More reactive hydrides require weaker acid [in fact, stronger acids decompose the hydrides, Eq. (12)] whereas less reactive hydrides [e.g., $\text{HCr}(\text{CO})_5^-$] require stronger acids. The dependence of product yields on pK_a is supportive of specific acid catalysis.

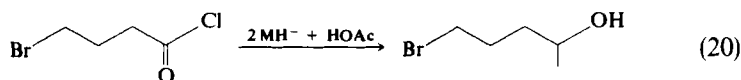
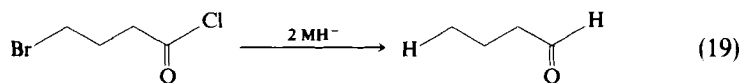
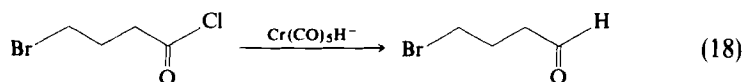
The rate of reduction of cyclohexanone by $\text{HCr}(\text{CO})_5^-/\text{HOAc}$ was not affected by added CO, nor did a 1:1 mixture of $\text{HCr}(\text{CO})_5^-$ and HOAc exchange bound ^{12}CO and free ^{13}CO . These results imply that metal coordination of the ketone or aldehyde is not a requirement. The first reaction path noted in Scheme 10, proceeding via a neutral dihydride, is *most likely less appropriate* for the group 6 metal hydrides than it might be for group 8 (i.e., metal hydrides more apt to form oxidative addition products). The other reactions of Scheme 10 represent an acid-assisted path appropriate for ketones and less reactive aldehydes, and a hydride transfer from more reactive hydrides to aldehydes. The final reaction in Scheme 10 could be appropriate for those hydrides in which the HOMO or negative charge



SCHEME 10

is localized on M. Such a path was proposed for the $\text{Et}_3\text{NH}^+\text{HFe}(\text{CO})_4^-$ reduction of aldehydes (106).

Finally, impressive selectivity has been demonstrated by the group 6 anionic hydrides. Equations (18)–(20) utilize 4-bromobutyral chloride to demonstrate selectivity for acid halide reduction. In the presence of 2 equivalents of $\text{HCr}(\text{CO})_5^-$ the C—Br bond will be reduced; however, if 1 equivalent of HOAc is added prior to addition of 2 equivalents of MH^- , the aldehyde is reduced preferentially. The $\text{HCr}(\text{CO})_5^-$ reduces acid chlorides in the presence of nitrobenzene (104), whereas if $\text{HFe}(\text{CO})_4^-$ is the reactive hydride the nitro group is preferentially reduced (102).



The $\mu\text{-HM}_2(\text{CO})_{10}^-$ anions are typically unreactive under conditions where the $\text{HM}(\text{CO})_5^-$ exhibit high reactivity. Nevertheless, $\mu\text{-HMo}_2(\text{CO})_{10}^-$ (107) and $\mu\text{-HCr}_2(\text{CO})_{10}^-$ (108) have been shown to selectively reduce the C=C bond of α - β unsaturated esters and ketones in the presence of a proton source in refluxing THF (temperatures where the dimers are expected to disrupt (38b)).

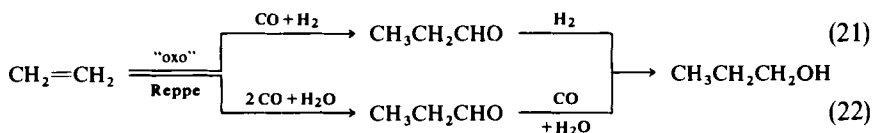
V

ANIONIC TRANSITION METAL HYDRIDES AS CATALYSTS

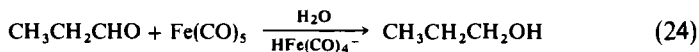
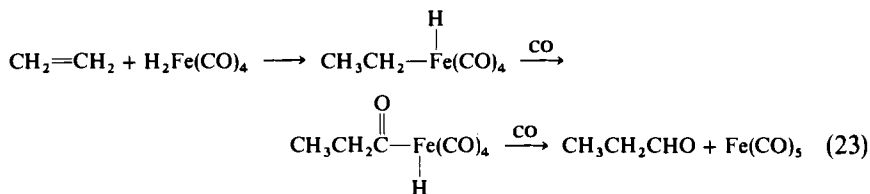
This section briefly reviews reports of anionic hydrides as catalysts. This is an extensive field, and our short discussion makes no claim of completeness.

The quintessential anionic hydride catalyst, in chronology, activity, and understanding of mechanistic pathway, is HCo(CN)_5^{3-} . This inexpensive hydride has been used for the catalytic reduction of organic halides, oximes, and nitro compounds and for selective hydrogenation of activated olefins. The remarkable catalytic activity as well as mechanistic studies by Professor J. Halpern (109) has been extensively reviewed (2,110).

Another inexpensive anionic hydride that has catalytic activity is HFe(CO)_4^- . It isomerizes olefins in the presence of additives (111) and is a catalyst or catalyst precursor in the Reppe modification of the oxo process [Eqs. (21) and (22)] (99). Clearly the utility of the iron carbonyl lies in its ability

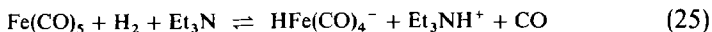


to undergo base attack and to serve as a catalyst for the water-gas shift reaction (Scheme I). In studies of the Reppe reaction using Fe(CO)_5 as catalyst, Pettit *et al.* (99) found that at pH levels above 11.0 the HFe(CO)_4^- anion predominated; however, no olefin consumption took place. Only at pH levels below 10.7 did alcohol form. A plausible explanation of the pH dependence is that the $\text{H}_2\text{Fe(CO)}_4$ formed at lower pH values is active at binding and activating the olefin as indicated in Eqs. (23) and (24) (112,113). The reduction of aldehyde to alcohol is presumed to be effected by HFe(CO)_4^- with H_2O as the proton source (106).



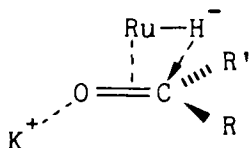
Studies of the hydrogenation of aldehydes and ketones using Fe(CO)_5 as catalyst found reactions to proceed well only in the presence of tertiary amines

as solvent (114). Radhi and Marko suggested that the amine, a relatively strong base, is necessary for the *heterolytic* activation of H_2 according to Eq. (25) (114). The rate of hydrogenation showed a dependence on H_2 pressure and a strong temperature dependence, operating only above $150^\circ C$, the temperature at which CO groups are labile (115).



Other reactions catalyzed by $HFe(CO)_4^-$ are as follows: Transfer hydrogenation of ketones to alcohols using an alcohol as hydrogen donor under phase-transfer conditions (116); the reduction of nitroarenes to anilines (99,117); the regiospecific reduction catalysis of annulenes under phase-transfer conditions (118); and the reduction of CO_2 to alkyl formates (119).

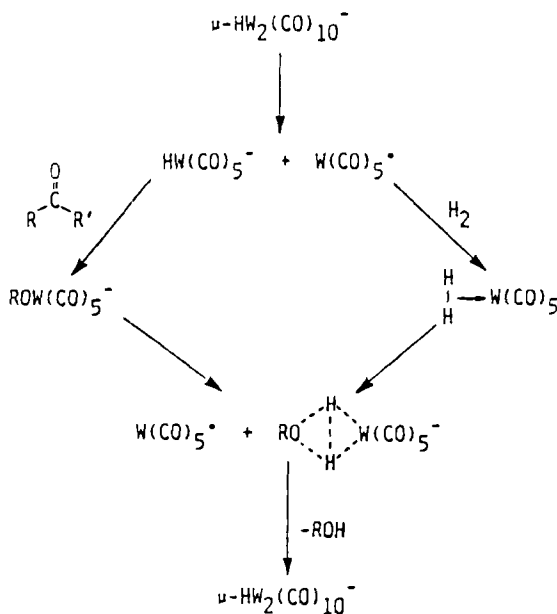
The anionic ruthenium hydrides $H_2Ru(PPh_3)_2PPh_2C_6H_4^-$ and $[(Ph_3P)_3-(Ph_2P)Ru_2H_4]^{2-}$ are catalysts or catalyst precursors for hydrogenation of ketones, nitriles, and esters (60,120,121). The observed counterion effects ($K^+ \cdot 18\text{-cr-6} > K^+ > K^+ \cdot \text{crypt-222}$) led the authors to propose cation assistance in a polar transition state or intermediate:



In fact there is an immediate conversion of the orthometallated dihydride to *fac*- $Ru(H)_3(PPh_3)_3^-$ in the presence of H_2 . Noted earlier, the X-ray structure of the $K^+ \cdot 18\text{-cr-6}$ salt of this hydride (17) shows distinct interaction of the cation with the *fac*- RuH_3 arrangement (62). The counterion effect might signify the stabilization of a more reactive trihydride. The $H_2Ru(PPh_3)_2PPh_2C_6H_4^-$ anion also catalyzes the selective hydrogenation of anthracene to 1,2,3,4-tetrahydroanthracene. The mechanism, demonstrated to involve anionic polyhydrides in the reaction pathway, has been studied by the Halpern group (61).

The group 6 bridging hydride complexes, $\mu\text{-}HM_2(CO)_{10}^-$ ($M = Cr, Mo, W$) have been used as catalyst precursors or implicated in catalytic cycles for hydrogenation of CO_2 (119,122), ketones (123,124), aldehydes (123,124), and Schiff bases (125). In that these species readily cleave upon heating (38b,43b), they offer entry into the formation of both coordinatively unsaturated species, $M(CO)_5^0$, and the highly reactive monomer, $HM(CO)_5^-$.

The metalloformate species, $HCO_2M(CO)_5^-$ is rapidly produced on addition of CO_2 to $HM(CO)_5^-$ (100,126-128). The formate complex is CO labile, and a dihydrogen adduct or a dihydride, $HCO_2M(CO)_4(\eta^2-H_2)^-$ or



SCHEME 11. (123).

$\text{HCO}_2\text{M}(\text{CO})_4(\text{H})_2^-$, respectively, may then undergo heterolytic cleavage of H_2 to produce HCO_2H and $[\text{HM}(\text{CO})_4]^-$. If the reaction is carried out in MeOH, methyl formate is the ultimate product (122).

In the hydrogenation of ketones and aldehydes, the superiority of the $\mu\text{-HM}_2(\text{CO})_{10}^-$ dimer as catalyst has suggested a role for both $\text{M}(\text{CO})_5^0$ and $\text{HM}(\text{CO})_5^-$ (123). The latter is suggested to add to the carbonyl functionality as in Eq. (16), and the former might be expected to bind H_2 (Scheme 11) (123). Additionally, $\mu\text{-HM}_2(\text{CO})_{10}^-$ has been considered an intermediate in the hydrogenations of ketones, aldehydes, and Schiff bases by $\text{M}(\text{CO})_6/\text{NaOMe}/\text{MeOH}$ systems (124,125). Again highly reactive $\text{HM}(\text{CO})_5^-$ anions are proposed intermediates.

As a final item we mention the mixed metal hydride $\text{HPt}(\text{SnCl}_3)_4^{3-}$ which is formed when PtCl_2 is dissolved in the molten salt $[\text{Et}_4\text{N}][\text{SnCl}_3]$ under H_2 pressure (2,129). This hydride is a catalyst for the hydrogenation of 1,5,9-cyclododecatriene to predominantly cyclododecene, ethylene to ethane, methyl linoleate to methyl oleate, and vinyl chloride to ethane. The catalyst is also active for the hydroformylation of ethylene to propionaldehyde and the carbomethoxylation of 1-hexene to methyl heptanoate and methyl 2-methylhexanoate.

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Transition Metal Complexes with Terminal Carbyne Ligands

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I

INTRODUCTION

The first compounds with a formal metal-carbon triple bond $[(X)(CO)_4M(\equiv CR)]$; $X = Cl, Br, I$; $M = Cr, Mo, W$; $R = Ph$] were reported by E. O. Fischer and co-workers in 1973 (1). Since that time, the field of transition metal carbyne complexes has developed tremendously. In addition to phenylcarbynes, complexes with the following carbyne R groups are now known: alkyl, aryl, alkenyl, alkynyl, hydrido, silyl, amino, phosphino, thio, seleno, and halogeno. And while the first carbyne complexes were those of group 6 metals (Cr, Mo, W), transition metals of groups 5 (Ta), 7 (Mn, Re), and 8 (Fe, Os) are all now known to stabilize carbyne ligands. In this article, the terms "carbyne" and "alkylidyne" will be used interchangeably when referring to compounds with a formal metal-carbon triple bond.

A few previous reviews of transition metal carbyne chemistry, with emphases on specific aspects of the field, have been published. Synthetic and structural carbyne chemistry developed by E. O. Fischer and co-workers has been summarized in eight reviews (2,3). Reactions of $Cp(CO)_2W(\equiv C-tolyl)$ with metal compounds, forming di- or tri-metal clusters, have been reviewed by F. G. A. Stone (4). A few limited reviews of carbyne chemistry are also available (5). This article attempts to cover comprehensively the chemistry of terminal carbyne complexes up to January, 1986. The results which were included in the earlier reviews are not discussed in detail here.

Although the purpose of this article is to cover the chemistry of molecular carbyne complexes, there is also much interest in them as models for species which are possibly present on metal surfaces in catalytic reactions (6). Surface-bound methine (CH) is a proposed intermediate in the Fischer-Tropsch synthesis (7), and alkylidyne groups are suggested as intermediates in heterogeneously catalyzed alkyne metathesis reactions (8,9). Recently, Nicholas (10) argued for the involvement of hydroxycarbyne species $M\equiv COH$ as intermediates in the catalytic hydrogenation of CO. Using this species, he

rationalizes the formation of alcohols and methyl formate. A mechanism for the formation of hydrocarbons from $M\equiv\text{COH}$ has also been proposed (11).

Although we make no attempt to survey the literature in this area, it is interesting to note that surface studies have yielded evidence for triply bridging CH , CCH_3 , and other alkylidyne fragments bound to single crystal faces (12). Such studies have shed some light on the mechanisms of heterogeneously catalyzed reactions over supported metals where such surface-bound fragments are proposed as possible intermediates (13).

II

BONDING, STRUCTURE, AND SPECTROSCOPIC PROPERTIES

A. Bonding

Molecular orbital calculations on carbyne complexes, e.g., $\text{Cp}(\text{CO})_2\text{Mn}(\equiv\text{CR})^+$ (14), $(\text{CO})_5\text{Cr}(\equiv\text{CH})^+$ (15), and *trans*- $\text{X}(\text{CO})_4\text{Cr}(\equiv\text{CR})$ (16), show that the metal-carbon triple bond consists of a σ and two π bonds (Fig. 1). In calculations for $(\text{CO})_5\text{Cr}(\equiv\text{CH})^+$, the HOMO of the CH^+ fragment is the sp -hybrid orbital on the carbon containing a pair of electrons; the LUMOs are the two degenerate p π orbitals on the carbon. The degenerate HOMOs of the $(\text{CO})_5\text{Cr}$ fragment are the d lone-pair orbitals. The LUMO is the $4sp$ -hybrid orbital of Cr (15). Donation from the HOMO of the carbyne ligand to the LUMO of the metal fragment creates a σ bond. Two π bonds are formed by back-donation from the two HOMOs of the metal fragment into the LUMOs of the carbyne. According to a CNDO calculation, the donor-acceptor properties of the methylcarbyne ligand in $\text{Cl}(\text{CO})_4\text{Cr}(\equiv\text{CMe})$ are similar to those of the NO radical (17). Molecular orbital calculations show that the rotational energy barrier around the $M\equiv\text{C}$ triple bond in $\text{Cp}(\text{CO})_2$

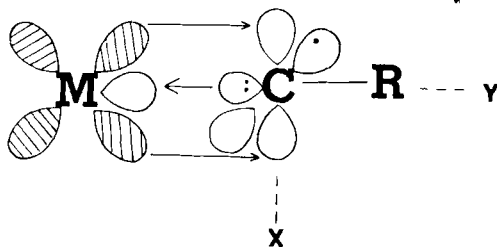


FIG. 1. Bonding of transition metals to terminal carbyne ligands. Another d orbital in the yz plane is omitted in this drawing.

$\text{Mn}(\equiv\text{CPh})^+$ and $(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_2\text{Cr}(\equiv\text{CPh})^+$ is low (2 kcal/mol) (18). These theoretical findings agree with ^{13}C -NMR studies of the complexes (18).

Cationic carbynes, e.g., $\text{Cp}(\text{CO})_2\text{Mn}(\equiv\text{CR})^+$, $(\text{CO})_5\text{Cr}(\equiv\text{CNet}_2)^+$, are frequently observed to undergo nucleophilic addition at the carbyne carbon (14). Molecular orbital studies of these compounds yield the result that the two LUMOs are antibonding π orbitals between the metal and carbyne carbon. Based on this, Kostić and Fenske have suggested that nucleophilic attack on a carbyne carbon atom is frontier orbital controlled with the nucleophile donating electron density from its HOMO (the "lone pair") to the LUMO of the carbyne (14,16).

Calculations indicate that the charge on the carbyne carbon is significantly negative, -0.42 for $\text{Cl}(\text{CO})_4\text{Cr}(\equiv\text{CH})$ and -0.31 even for the cationic carbyne complex $(\text{CO})_5\text{Cr}(\equiv\text{CH})^+$, due to the great π -acidity of the carbyne ligand (15). Because of the negative charge on the carbyne carbon, it seems likely that nucleophilic additions to carbyne ligands are not charge controlled but frontier orbital controlled. Protons have been observed to add to the carbyne carbon atom in neutral carbyne compounds (19). The protonation reactions are suggested to be charge controlled (19). Reactions of carbynes with various nucleophiles and electrophiles will be discussed in depth in Section IV.

B. Structure

X-Ray structure determinations of carbyne complexes show that they have very short metal-carbon bond lengths consistent with a metal-carbon triple bond. Carbyne compounds which have been structurally characterized are listed in Table I.

Metal- $\text{C}_{\text{carbyne}}$ distances are shorter than the metal- $\text{C}_{\text{carbene}}$ and metal- $\text{C}_{\text{carbonyl}}$ distances in related compounds; for example, the $\text{Cr}-\text{C}_{\text{carbyne}}$ distance (1.69 Å) in $\text{I}(\text{CO})_4\text{Cr}(\equiv\text{CMe})$ (24) is shorter than the $\text{Cr}-\text{C}_{\text{carbonyl}}$ distance (1.95 Å) in this compound and shorter than the $\text{Cr}-\text{C}_{\text{carbene}}$ distance (2.09 Å) in $(\text{CO})_5\text{Cr}[\equiv\text{C}(\text{Me})(\text{NHMe})]$ (24). The $\text{Cr}-\text{C}_{\text{aminocarbyne}}$ distance (1.72 Å) in $\text{Br}(\text{CO})_4\text{Cr}(\equiv\text{CNet}_2)$ (34) is longer than the $\text{Cr}-\text{C}_{\text{carbyne}}$ distance (1.68 Å) in $\text{Br}(\text{CO})_4\text{Cr}(\equiv\text{CPh})$ (27). This lengthening is due to delocalization of electron density from the nitrogen p orbital by interaction with a p orbital on the carbyne carbon atom (Fig. 2) (14,38). The $\text{C}_{\text{carbyne}}-\text{N}$ bond lengths in

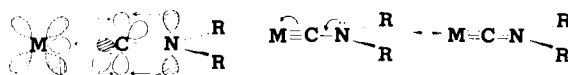


FIG. 2. Resonance representation of interaction between p orbitals of carbon and nitrogen in $\text{M}\equiv\text{CNR}_2$.

TABLE I
 CARBYNE COMPLEXES: SOME STRUCTURAL PARAMETERS^a

$L_n M \equiv C - R$	$M \equiv C$ distance (Å)	$M \equiv C - R$ angle (°)	Ref.
$(Me_3CCH_2)_3Ta(\equiv CMe_3) \cdot Li(dmp)^b$	1.76(2)	165(1)	20
$(dmp)_2(H)Ta(\equiv CMe_3)(ClAlMe_3)^c$	1.850(5)	178.7(4)	21
$(\eta^5-C_5Me_5)(PMe_3)_2(Cl)Ta(\equiv CPh)$	1.849(8)	171.8(6)	22
$trans-(Cl)(CO)_4Cr(\equiv CMe)$	1.710	179.26	23
$trans-(I)(CO)_4Cr(\equiv CMe)$	1.69(1)	180	24
$mer-(Br)(CO)_3(PMe_3)Cr(\equiv CMe)$	1.68(3)	177(3)	24
$[trans-(PMe_3)(CO)_4Cr(\equiv CMe)]BCl_4$	1.67	175	3
$(CO)_4Cr[\equiv C-(cyclopropyl)](\mu-Br)Cr(CO)_5$	1.71(1)	178(2)	25
$trans-(Br)(CO)_4Cr[\equiv C-(cyclo-3,6-Me, i-Pr, C_6H_9)]$	1.67	173.63	26
$trans-(Br)(CO)_4Cr(\equiv CPh)$	1.68(3)	180(0)	27
$trans-(Cl)(CO)_4Cr(\equiv CPh)$	1.68(1)	180(0)	27
	1.728(4)	180 ^d	28
$(Br)[P(OPh)_3]_2(CO)_2Cr(\equiv CPh)$	1.68(1)	174(1)	29
$(Br)(t-BuNC)_2(CO)_2Cr(\equiv CPh)$	1.76(3)	171(2)	29
$trans-(Br)(CO)_4Cr[\equiv C-(4-C_6H_4CF_3)]$	1.68(2)	171(3)	30
$trans-(Br)(CO)_4Cr[\equiv C-(ferrocenyl)]$	1.71(2)	175(2)	31
$trans-(I)(CO)_4Cr[\equiv C-(1-cyclopentyl)]$	1.65(2)	176(2)	32
$Cp(CO)_2Cr(\equiv C-CPh=CPh-C\equiv)Cr(CO)_2Cp$	1.707(2)	173.9(2)	33
$trans-(Br)(CO)_4Cr(\equiv CNEt_2)$	1.72(1)	177.2	34
$trans-(Ph_3Sn)(CO)_4Cr(\equiv CNEt_2)$	1.74(1)	177(1)	35
$trans-[(4-C_6H_4F)Se](CO)_4Cr(\equiv CNEt_2)$	1.75(1)	175(1)	36
$mer-(Br)(CO)_3(PPh_3)Cr(\equiv CNEt_2)$	1.75(1)	173(1)	37,38
$[(CO)_5Cr(\equiv CNEt_2)]BF_4$	1.797(9)	175.8(8)	38,39
$[trans-(CO)_4(PPh_3)Cr(\equiv CNEt_2)]BF_4$	1.76(1)	175(2)	37,38
$\{Cp(H)[P(OMe)_3]_2Mo(\equiv C-CH_2CMe_3)\}BF_4$	1.798(2)	170.02	19
$Mo(\equiv C-SiMe_3)(dppe)(Br)^e$	1.82(1)	174.2(7)	40
$trans-[(CO)_5Re]Mo(\equiv CPh)(CO)_4$	1.84(3)	N.R.	41
$(\mu-NCO)_2[(CO)_3Mo(\equiv CNEt_2)]_2$	1.82(2)	174(1)	42
$(\mu-I)_2[(CO)_3Mo(\equiv CNEt_2)]_2$	1.80(2)	172(1)	42
$[HB(3,5-Me_2-C_3HN_2)_3](CO)_2Mo[\equiv C-S-(4-C_6H_4NO_2)]$	1.801(4)	179.5(2)	43
$[B(C_3H_3N_2)_4](CO)_2Mo(\equiv CCl)$	1.894(9)	172.01	44
$trans-Br(CO)_4W(\equiv CMe)$	1.82(4)	178(4)	45
$trans-I(CO)_4W(\equiv CMe)$	1.77(4)	180	45
$trans-(Me)(PMe_3)_4W(\equiv CMe)$	1.89(3)	N.R.	46
$[(t-BuO)_3W(\equiv CMe)]_2$	1.759(6)	179.8(6)	47
$(Cl)_2(PEt_3)_2(PPhH)W(\equiv CMe_3)$	1.808	173.90	48
$W(\equiv CMe_3)(=CHCMe_3)(CH_2CMe_3)(dmp)^c$	1.785(8)	175.3(7)	49
$\{W[\eta^5-C_5Me_4(t-Bu)](\equiv CMe_3)I\}(\mu-N_2H_2)$	1.769(8)	171.9(7)	50
$Cp(CO)_2W(\equiv C-SiPh_3)$	1.82(2)	176(1)	51
$trans-(I)(CO)_4W(\equiv CPh)$	1.90(5)	162(4)	24
$trans-(Cl)(CO)_4W(\equiv CPh)$	2.02	173	3
$(CO)_4Co-W(\equiv CPh)(CO)_4$	1.82(1)	176(1)	52
$Br(CO)_2(py)_2W(\equiv CPh)$	1.84(2)	173.8(6)	53

(continued)

TABLE I (continued)

$L_n M \equiv C - R$	M \equiv C distance (Å)	M \equiv C—R angle ($^\circ$)	Ref.
Cp(CO) ₂ W(\equiv C—tolyl)	1.82(2)	176(2)	54
[B(C ₃ H ₃ N ₂) ₄](CO) ₂ W(\equiv C—tolyl)	1.821(7)	164.0(6)	55
<i>trans</i> -Br(CO) ₄ W(\equiv C—(4-C ₆ H ₄)—C \equiv)W(CO) ₄ Br	1.89(3)	176(3)	56
<i>trans</i> -Cl(CO) ₄ W(\equiv C—[C ₆ H ₅ Cr(CO) ₃])	1.84(3)	174(2)	57
[(CO) ₅ W(\equiv CNEt ₂)]SbCl ₆	1.90(3)	173(3) ^f	58
	1.80(3)	171(2)	58
(μ -SPh) ₂ [(CO) ₃ W(\equiv CNEt ₂)] ₂	1.82(2)	172(2)	42
(μ -N ₃) ₂ [(CO) ₃ W(\equiv CNEt ₂)] ₂	1.75(4)	176(3)	42
[(<i>t</i> -BuO) ₃ W(\equiv CNMe ₂)] ₂	1.76(2)	179(2)	59
[W ₂ (\equiv CPMe ₃) ₂ (PMe ₃) ₄ (Cl) ₄][AlCl ₄] ₂	1.83(3)	174(2)	60
Cp(PPh ₃)(CO)W(\equiv CSPH)	1.807(10)	174.2(6)	61
W(\equiv CH)(Cl)(PMe ₃) ₄	1.84	N.R.	62
[Cp(CO) ₂ Mn(\equiv C—CH=CPh ₂)]BF ₄	1.665(5)	174.6(4)	63
(I) ₂ (py) ₂ Re(\equiv CCMe ₃)(CHCMe ₃)	1.742(9)	174.8(7)	64
[(dppe) ₂ (Cl)Re(\equiv CNHMe)]BF ₄ ^e	1.80(3)	175(2)	65
{(PPh ₃)(CO) ₃ Fe(\equiv CN(<i>i</i> -Pr) ₂)} ₂ BCl ₄	1.734(6)	N.R.	66
(Cl)(CO)(PPh ₃) ₂ Os(\equiv C—tolyl)	1.77(2)	164(2)	67
(PPh ₃) ₂ (Cl) ₂ (SCN)Os(\equiv C—(4-C ₆ H ₄ NMe ₂))	1.75(1)	N.R.	68
{(PPh ₃) ₂ (Cl) ₂ [(tolyl)NC]Os(\equiv C—(4-C ₆ H ₄ NMe ₂))} ₂ ClO ₄	1.78(1)	N.R.	68

^a Compounds are ordered by groups in the periodic table. N.R., Not reported.

^b dmp = *N,N'*-Dimethylpiperazine.

^c dmpe = PMe₂CH₂CH₂PMe₂.

^d Result of neutron diffraction study.

^e dppe = PPh₂CH₂CH₂PPh₂.

^f Two different crystals.

Br(CO)₄Cr(\equiv CNEt₂) (34) and [(CO)₅Cr(\equiv CNEt₂)]BF₄ (39) are 1.29 and 1.27 Å, respectively, and fall in the range observed for carbon–nitrogen double bonds (1.28 Å). The M \equiv C—R moiety is observed to be nearly linear in most cases (Table I). However, a distinct bend in the M \equiv C—R angle is seen in a few examples, e.g., *trans*-I(CO)₄W(\equiv CPh) (162°), Cl(CO)(PPh₃)₂Os(\equiv C—tolyl) (164°), and *mer*-Br(CO)₃(PPh₃)Cr(\equiv CNEt₂) (173°); these deviations from linearity have been attributed to low symmetry of the carbyne π electron clouds, crystal packing forces, or nonbonding interactions (16).

C. Spectroscopic Properties

The most commonly used technique for the characterization of carbyne complexes is ¹³C-NMR spectrometry; ¹³C chemical shifts of some carbyne compounds are tabulated in References 2 (E. O. Fischer and U. Schubert), 60,

69, and 70. Generally these resonances occur at very low fields ranging from 235 ppm [$\text{I}(\text{CO})_4\text{W}(\equiv\text{CNMe}_2)]$ (2) to 401 ppm [$\text{W}(\equiv\text{CCMe}_3)(\text{PMe}_3)_3\text{Cl}_3$] (69), overlapping the carbene region (190–400 ppm) (71). The chemical shift depends on the electron-donating ability of the carbyne R substituents; for example, in $(\text{Br})(\text{CO})_4\text{W}(\equiv\text{CR})$, the carbyne resonance moves from high to low field with changes in R in the order $(2)\text{NMe}_2$ (236 ppm) > Ph (271 ppm) > CH_3 (288 ppm). Tungsten carbyne compounds show $^{183}\text{W}-^{13}\text{C}$ coupling constants in the range 160–300 Hz, which is greater than the $^{183}\text{W}-^{13}\text{C}$ coupling constants (80–140 Hz) of carbene compounds (70,72).

Infrared and Raman spectra of carbyne complexes show absorptions characteristic of the metal–carbon triple bond stretching vibration (67,73–77); in the *trans*- $\text{X}(\text{CO})_4\text{M}(\equiv\text{CR})$ (R = Me, Ph; X = Cl, Br, I, Re(CO)₅; M = Cr, Mo, W) complexes, this $\nu(\text{M}\equiv\text{C})$ frequency occurs in the range 1250–1380 cm^{-1} . Its value decreases with the metal in the order $\text{W} > \text{Cr} > \text{Mo}$ (76), and it is higher for the phenyl than the methyl carbynes. The stretching force constant for the $\text{W}\equiv\text{C}$ bond in $\text{X}(\text{CO})_4\text{W}(\equiv\text{CCH}_3)$ (X = Cl, Br, I) is calculated to be 7.4 mdyn \AA^{-1} (73). The C–N stretching frequencies of the aminocarbyne compounds $\text{X}(\text{CO})_4\text{W}(\equiv\text{CNR}_2)$ and $[(\text{CO})_5\text{Cr}(\equiv\text{CNEt}_2)]\text{BF}_4$ appear around 1650 cm^{-1} which is the region for $\nu(\text{C}=\text{N})$ of $\text{C}=\text{N}$ double bonds (78,79). Raman studies of these aminocarbyne compounds also support delocalization (Fig. 2) of electron density from nitrogen to the carbyne carbon, i.e., the metal–carbon bond order is calculated to be 2.2 (79).

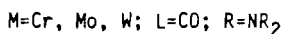
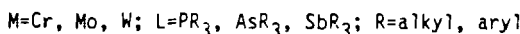
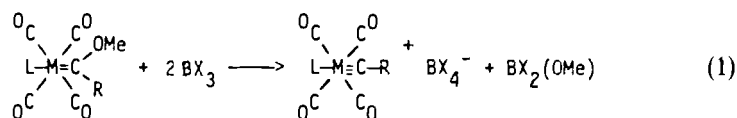
The carbyne complexes $\text{X}(\text{CO})_2\text{L}_2\text{W}(\equiv\text{CPh})$ (X = Cl, Br, I; L_2 = TMEDA, bpy, (py)₂, diphos) are luminescent at room temperature in fluid solution when irradiated with visible light (80). The excited state is associated with an absorption band centered at 22,030 cm^{-1} which is assigned to a d -metal $\rightarrow \pi^*$ -alkylidyne transition (80).

III

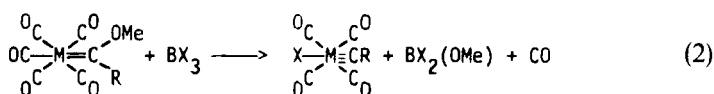
SYNTHESIS OF CARBYNE COMPLEXES

A. Lewis Acid-Assisted Abstraction

Lewis acid-assisted abstraction was the method used by Fischer (1) to prepare the first carbyne complexes. It involves removal of the alkoxy group from an alkoxy carbene ligand using boron trihalides BX_3 (X = F, Cl, Br) at low temperatures [Eq. (1)] (2). Since the carbyne ligand is a good π acceptor, it reduces back-bonding to the other ligands, particularly to the *trans* ligand L. When L is a relatively poor π acceptor (e.g., PR_3 , AsR_3 , SbR_3), the cationic carbyne complexes are stable and can be isolated [Eq. (1)].



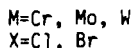
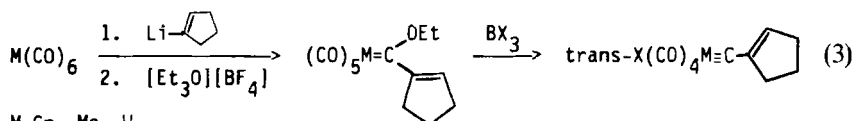
However, when L is a strong π acceptor, e.g., CO, its bond to the metal is weakened, and it is readily replaced by a halide to give the neutral *trans*-halo carbyne complex [Eq. (2)] (2). One type of cationic carbyne complex

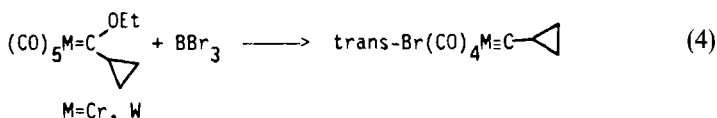


$[(\text{CO})_5\text{M}(\equiv\text{CR})]\text{BF}_4$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) can be isolated at -100°C according to Eq. (1) when R is an amino group (NR_2) (34,42,58); delocalization (Fig. 2) of electron density from the nitrogen to the carbyne carbon makes this carbyne ligand less π -accepting thus allowing the $(\text{CO})_5\text{M}(\equiv\text{CNR}_2)^+$ complexes to exist at low temperature. However, these aminocarbyne compounds $[(\text{CO})_5\text{M}(\equiv\text{CNR}_2)]\text{BF}_4$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) are quite thermally labile; even the weakly coordinating BF_4^- replaces a CO to give *trans*-(BF_4)(CO) $_4$ - $\text{M}(\equiv\text{CNR}_2)$ (42,58).

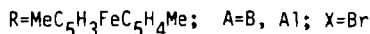
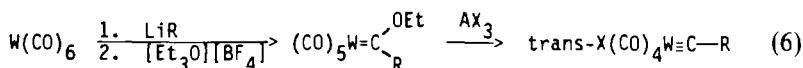
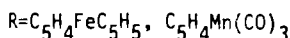
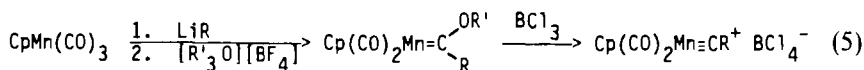
E. O. Fischer and co-workers have reviewed the preparations of carbyne compounds using the Lewis acid-assisted abstraction method (2). In addition to alkoxy groups, alkythio, amino, siloxy, and acetoxy groups can be removed by Lewis acids (2). Beside the aforementioned boron halides, halides of aluminum and gallium can be used as Lewis acids for these reactions (2). The carbyne complexes $[\text{L}_n\text{M}(\equiv\text{CR})]$ with the following R groups have been prepared using this method (2): alkyl, aryl, vinyl, acetylenic, metallocenyl, amino, and silyl.

A recent example of this method gives a cyclopentenyl carbyne complex [Eq. (3)] (32). A cyclopropyl carbyne complex is prepared similarly [Eq. (4)] (25). On heating, the cyclopropyl chromium carbyne ($> -30^\circ\text{C}$)

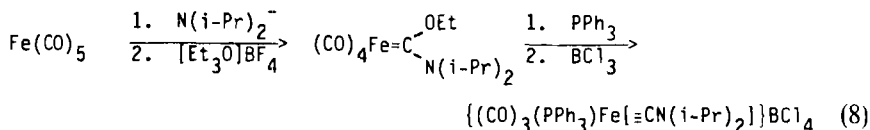
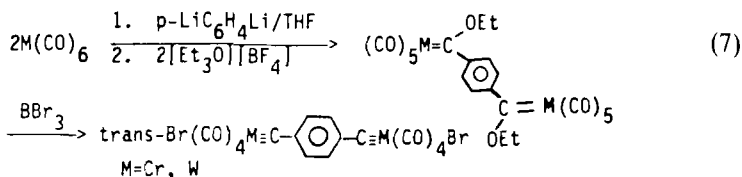




is converted to the bromide-bridged dichromium complex $(\text{CO})_5\text{Cr}(\mu\text{-Br})\text{Cr}(\equiv\text{C-cyclopropyl})(\text{CO})_4$ (25). Ferrocenyl or ruthenocenyl carbyne complexes are prepared using the same method [Eqs. (5) and (6)] (31,81). The tricarbonylchromium- η^6 -phenyl carbynes $\text{trans-X}(\text{CO})_4\text{M}\{\equiv\text{C}-[\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3]\}$ ($\text{M} = \text{Cr}, \text{W}$; and $\text{X} = \text{Cl}, \text{Br}$) are obtained in a similar reaction (82).



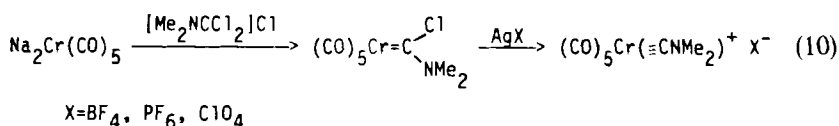
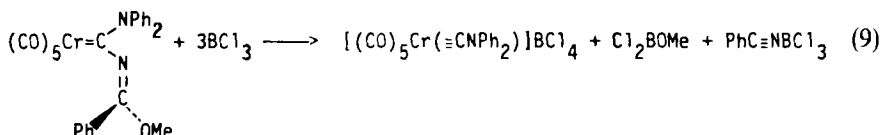
A dinuclear biscarbyne is prepared using dilithiated benzene according to Eq. (7) (56). Recently, Fischer and co-workers succeeded in preparing the first iron carbyne using a similar method [Eq. (8)] (66). An X-ray structural inves-



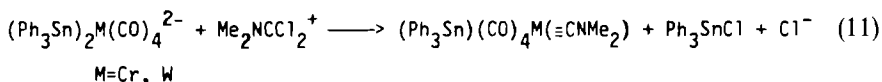
tigation of the product shows that the iron has a distorted trigonal bipyramidal geometry with the triphenylphosphine and one carbonyl ligand in the apical positions (66).

Due to the low nucleophilicity of NPh_2^- , diaryl aminocarbene compounds $(\text{CO})_5\text{M}[\equiv\text{C}(\text{NPh}_2)(\text{OR})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) cannot be prepared by the

method in Eq. (8). However, they may be prepared using the new route given in Eq. (9) (83,84). Abstraction of the Cl^- with Ag^+ from a chloroaminocarbene compound is also a useful synthetic route to the relatively unstable amino-carbyne compound in Eq. (10) (85).



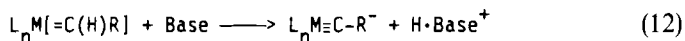
Reactions of the dianions $(\text{Ph}_3\text{Sn})_2\text{M}(\text{CO})_4^{2-}$ ($\text{M} = \text{Cr}, \text{W}$) with $\text{Me}_2\text{NCCl}_2^+$ produce amino carbyne compounds according to Eq. (11) (86). By analogy with Eq. (10), a seven-coordinate $(\text{Ph}_3\text{Sn})_2(\text{CO})_4\text{M}[\equiv\text{C}(\text{Cl})(\text{NMe}_2)]$ intermediate was proposed; the triphenyltin group functions as a chloride acceptor.



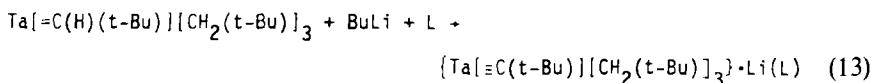
B. α -Hydrogen Abstraction/ α -Hydrogen Migration

1. α -Hydrogen Abstraction by Base

In certain cases, α -protons of an alkylidene ligand may be abstracted by a base to give alkylidyne compounds [Eq. (12)]. These abstractions are useful for the preparation of a variety of carbynes.



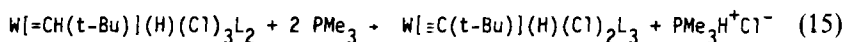
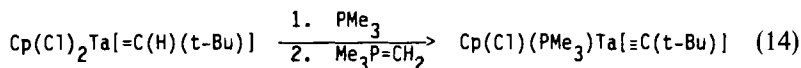
The BuLi abstraction of a proton from a neopentylidene ligand to yield a neopentylidyne compound is illustrated in Eq. (13) (20). An X-ray structural



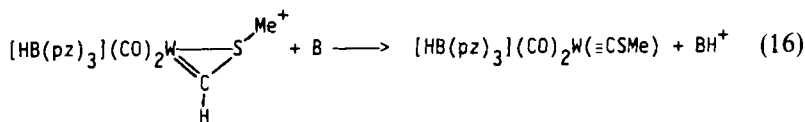
$\text{L} = \text{N}, \text{N}'\text{-dimethylpiperazine}$

analysis of the product shows that the Li^+ interacts strongly (2.19 Å) with the carbyne carbon and weakly (2.48 Å) with the α -carbon of one of the neopentyl ligands (20). A Wittig reagent is the base used in the conversion

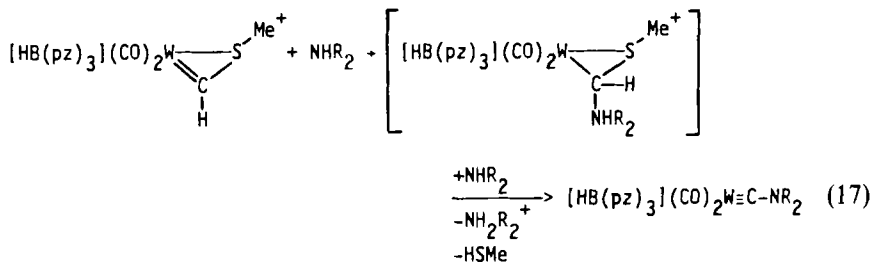
of a neopentylidene to a neopentylidyne ligand [Eq. (14)] (87). A related reaction involving α -hydrogen elimination but with loss of HCl occurs in the reaction of $W[=CH(t-Bu)](H)(Cl)_3L_2$ ($L = PMe_3$) with PMe_3 [Eq. (15)] (88).



Deprotonation of an η^2 -hydridothiocarbene produces a thiocarbene compound, although in low yield (10%) [Eq. (16)] (11). Deprotonation of the



methine hydrogen in a carbene adduct $[HB(pz)_3](CO)_2W[\eta^2-CH(SMe)(PEt_3)]^+$ with NaH, however, gives the thiocarbene compound in 90% yield (89). Reaction of the η^2 -thiocarbene with HNR_2 gives the amino-carbyne compound $[HB(pz)_3](CO)_2W(\equiv CNR_2)$ [Eq. (17)] (89). Even though there



is no direct evidence for it, an amine adduct is proposed as an intermediate. Deprotonation of the ammonium proton with free amine followed by elimination of HSMc would lead to the product.

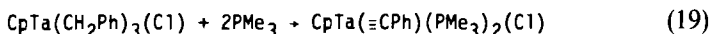
2. α -Hydrogen Migration

Migration of an α -hydrogen from an alkylidene ligand has been observed in several reactions reported by R. R. Schrock and co-workers; this process can be promoted by adding phosphine ligands. Thus, when PMe_3 is added to $CpTa[=C(H)(t-Bu)][CH_2(t-Bu)](Cl)$, the carbyne com-

plex $\text{CpTa}[\equiv\text{C}(t\text{-Bu})](\text{PMe}_3)_2\text{Cl}$ is formed [Eq. (18)] (87). This reaction has been suggested to occur by PMe_3 addition to the starting neopentylidene to give a pseudo-five-coordinate complex which undergoes intramolecular α -hydrogen transfer to give neopentane and the carbyne product.

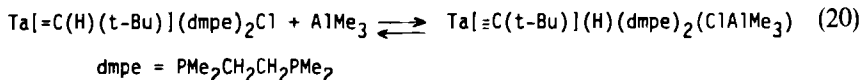


Reaction of $\text{CpTa}(\text{CH}_2\text{Ph})_3(\text{Cl})$ with PMe_3 affords the phosphine addition product $\text{CpTa}(\text{CH}_2\text{Ph})_3(\text{Cl})(\text{PMe}_3)$ which on heating yields the tantalum carbyne complex according to Eq. (19) (87). Whether this reaction proceeds



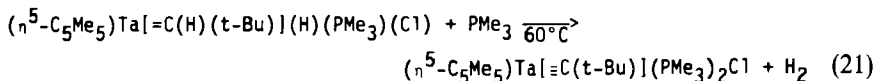
via a carbene intermediate has not been proven. However, since alkylidenes of tantalum have been prepared by α -hydrogen migration from an alkyl ligand (90), this assumption seems reasonable.

In certain alkylidene complexes such as $\text{CpTa}[\equiv\text{C}(\text{H})(t\text{-Bu})](\text{dmpe})_2\text{Cl}$, the neopentylidene ligand is grossly distorted toward a neopentylidyne hydride structure, as evidenced by the low values for ν_{CH_α} (2200 cm^{-1}) and J_{CH_α} (57 Hz) (21). Addition of AlMe_3 to this complex generates an aluminum-stabilized neopentylidyne hydride product [Eq. (20)] (21). The starting com-

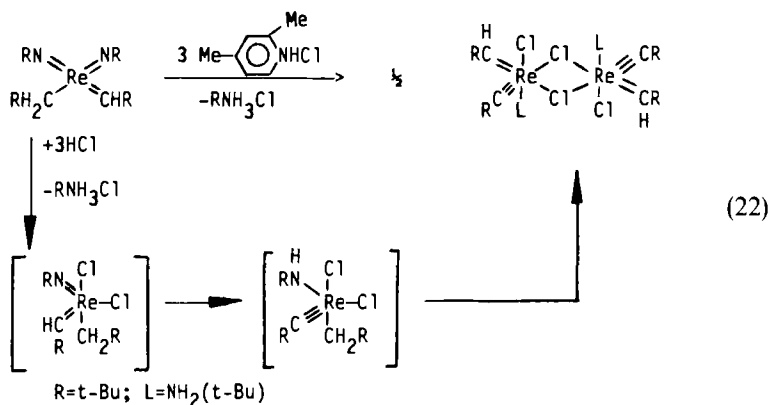


plex and product are in rapid equilibrium on the NMR time scale. An X-ray structure analysis of the carbyne complex shows that the tantalum atom has pentagonal bipyramidal coordination geometry with the two dmpe ligands and the hydride in the equatorial plane. The neopentylidyne and Cl-AlMe_3^- ligands occupy the two axial sites.

The neopentylidene group in $(\eta^5\text{-C}_5\text{Me}_5)\text{Ta}[\equiv\text{C}(\text{H})(t\text{-Bu})](\text{H})(\text{PMe}_3)\text{Cl}$ is also distorted ($J_{\text{CH}_\alpha} = 72\text{ Hz}$, $\nu_{\text{CH}_\alpha} = 2525\text{ cm}^{-1}$, and $\nu_{\text{TaH}} = 1730\text{ cm}^{-1}$) (91). Heating this compound in the presence of PMe_3 gives the neopentylidyne product [Eq. (21)] (91); the hydride acts as a leaving group and eliminates H_2 .

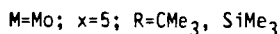
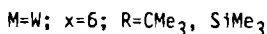
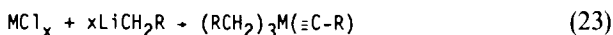


A rhenium neopentylidyne complex is obtained from the reaction of $\text{Re}[\equiv\text{C}(\text{H})(t\text{-Bu})][\text{CH}_2(t\text{-Bu})][\text{N}(t\text{-Bu})]_2$ with 3 equivalents of 2,4-lutidine hydrochloride according to [Eq. (22)] (64,92); it is proposed that the initial step involves protonation of an imido ligand, resulting in the loss of $t\text{-BuNH}_3^+$ and formation of $\text{Re}[\equiv\text{CH}(t\text{-Bu})][\text{CH}_2(t\text{-Bu})][\text{N}(t\text{-Bu})](\text{Cl})_2$.

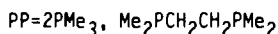
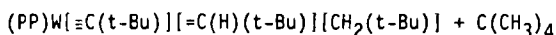


Proton transfer from carbon to nitrogen in this intermediate followed by dimerization would lead to the final product. This plausible sequence of reactions is based in part on the fact that if pyridine hydrochloride is used instead of 2,4-lutidine hydrochloride, the product is an unstable pyridine adduct of $\text{Re}[\equiv\text{C}(\text{t-Bu})][\text{CH}_2(\text{t-Bu})][\text{NH}(\text{t-Bu})](\text{Cl})_2$, which decomposes to the final product $\{ \text{Re}[\equiv\text{C}(\text{t-Bu})][=\text{C}(\text{H})(\text{t-Bu})][\text{NH}_2(\text{t-Bu})](\text{Cl})_2 \}_2$.

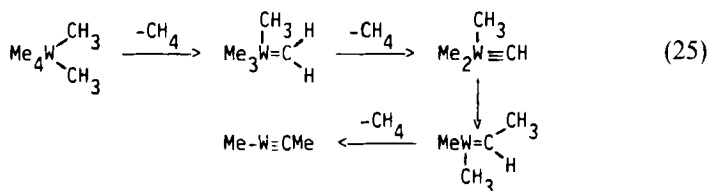
Reaction of WCl_6 with 6 equivalents of LiCH_2R ($\text{R} = \text{CMe}_3$ or SiMe_3) yields a tungsten carbyne complex [Eq. (23)] (93,94). Since W(VI) is reduced



by LiCH_2R , this reaction is not a straightforward double α abstraction (neopentyl \rightarrow neopentylidene \rightarrow neopentylidyne). MoCl_5 reacts similarly to give the corresponding Mo complex [Eq. (23)]. Heating the tungsten complex $\text{W}[\equiv\text{C}(\text{t-Bu})][\text{CH}_2(\text{t-Bu})]_3$ with 2 mol of PMe_3 or bis(dimethylphosphino)ethane gives a remarkable complex which contains alkyl, carbene, and carbyne ligands within the same molecule [Eq. (24)] (93).

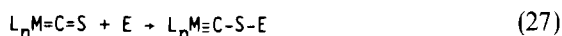
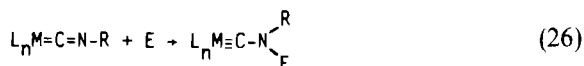


Wilkinson and co-workers reported the photolytic reaction of $(\text{PMe}_3)\text{WMe}_6$ with PMe_3 to give the carbyne complex *trans*-(Me)(PMe_3) $_4\text{W}(\equiv\text{CMe})$ (46). They proposed that two α -hydrogen-methyl eliminations afford a methylidyne alkyl intermediate. Then, methyl transfer to the methylidyne followed by α -hydrogen-methyl elimination results in the final product [Eq. (25)] (46).

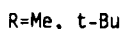
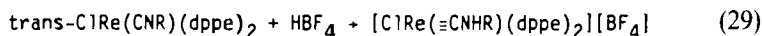
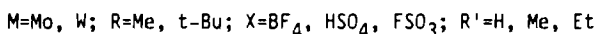
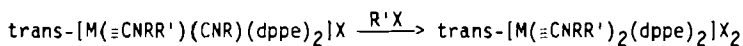
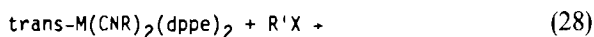


C. Electrophilic Addition to Isonitrile and Thiocarbonyl Ligands

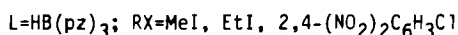
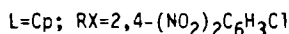
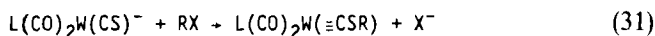
Addition of electrophiles to terminal isonitrile (CNR) ligands gives aminocarbyne complexes [Eq. (26)]; the analogous reaction of terminal thiocarbonyl (CS) ligands gives thiocarbynes [Eq. (27)]. These types of carbyne



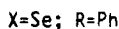
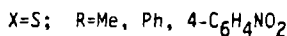
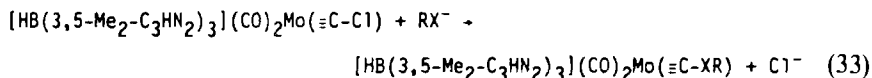
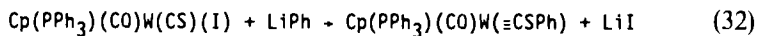
syntheses have been discussed in the Schubert review in Reference 2. The nitrogen of an isonitrile ligand in electron-rich metal complexes such as *trans*-M(CNR)₂(dppe)₂ (M = Mo, W) and (Cl)Re(CNR)(dppe)₂ is susceptible to electrophilic attack by H⁺ and alkylating agents to give the corresponding aminocarbyne compounds [Eqs. (28) and (29)] (65,95–100).



The thiocarbonyl ligand can be alkylated in complexes that are sufficiently electron-rich that their $\nu(\text{CS})$ values are less than approximately 1200 cm⁻¹. Thus, thiocarbyne complexes have been prepared as in Eqs. (30) and (31)

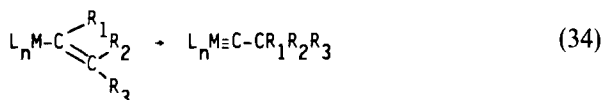


(101–103). A surprising route to thiocarbynes is the addition of Ph^- to the sulfur atom of a CS ligand [Eq. (32)] (61). This reaction probably proceeds by a mechanism involving radicals. Substitution of Cl^- in a chlorocarbene with XR^- ($\text{X} = \text{S}, \text{Se}$) is also a useful route to thio- and selenocarbene compounds [Eq. (33)] (43).

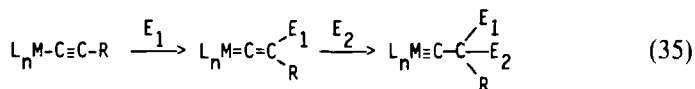


D. Transformations of Vinyl, Vinylidene, Acetylene, and Acetylde Complexes into Carbynes

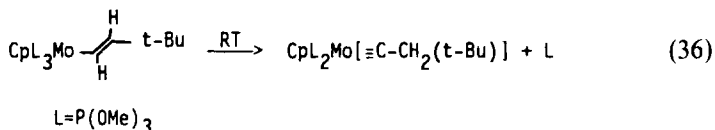
Vinyl ligands may rearrange into carbynes according to Eq. (34). Vinylidene ligands may be converted to carbynes by reaction with electrophiles at the β -

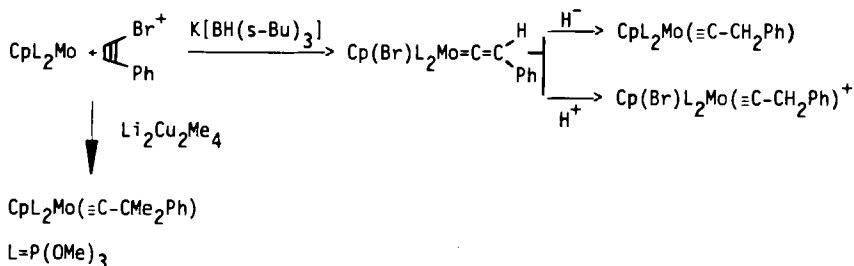


carbon [Eq. (35)]; double β -additions of electrophiles to an acetylde ligand also lead to carbynes [Eq. (35)]. These transformations are useful synthetic routes to molybdenum and tungsten carbynes.



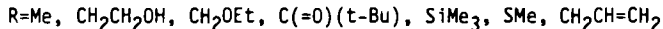
In benzene solution and also in the solid state, the vinyl complex $\text{CpL}_3\text{Mo}-\text{CH}=\text{CH}(t\text{-Bu})$, in the only reported rearrangement of this type, forms the carbene compound $\text{CpL}_2\text{Mo}[\equiv\text{C}-\text{CH}_2(t\text{-Bu})]$ with loss of an L ligand [Eq. (36)] (104). The rearrangement is suppressed by added $\text{P}(\text{OMe})_3$, suggesting that a vacant coordination site is required for the H shift to occur (104).



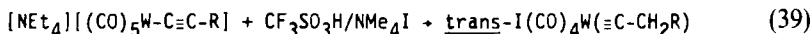
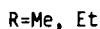
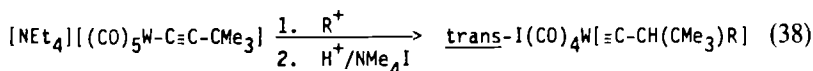


SCHEME 1

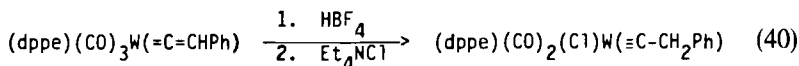
Vinylidene ligands have been converted to carbynes by reaction with H^- or H^+ as shown in Scheme 1 (105). The precursor acetylene complex is converted to the carbyne complex by reaction with $\text{Li}_2\text{Cu}_2\text{Me}_4$ (Scheme 1) (105). This reaction was proposed to go via the intermediate vinylidene complex $\text{Cp}(\text{Br})\text{L}_2\text{Mo}(=\text{C}=\text{CMePh})$, which would undergo nucleophilic attack by Me^- to give the carbyne product. Green and co-workers have reported the reaction of an anionic vinylidene complex with various alkyl halides to yield new carbynes [Eq. (37)] (106).



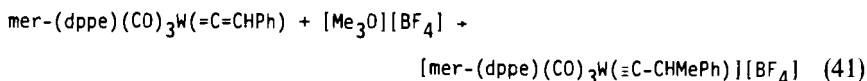
Based on molecular orbital calculations (107), it was suggested that electrophiles (E^+) should add to the β -carbon atom of acetylide ligands to give vinylidenes. Addition of a second electrophile should also occur at the β -carbon, yielding a carbyne ligand [Eq. (35)]. Such double β -additions of electrophiles to acetylide ligands have indeed been observed to give carbynes [Eqs. (38) and (39)] (108).



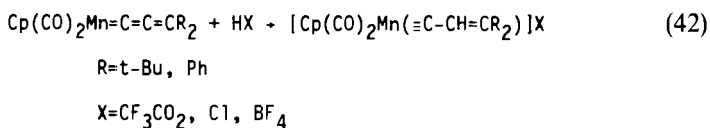
Protonation of a vinylidene ligand also leads to the formation of a carbyne according to Eq. (40) (109). Similarly, addition of Me^+ to the vinylidene



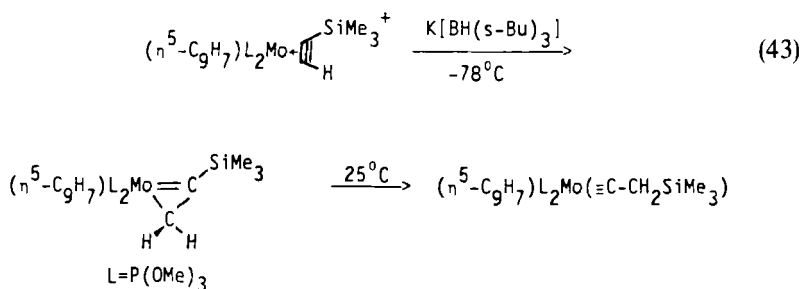
compound in Eq. (41) produces the corresponding cationic carbyne (110). An interesting extension of the reaction of vinylidenes with electrophiles is the



protonation of the β -carbon in an allenylidene ligand to yield a vinylcarbyne [Eq. (42)] (63).

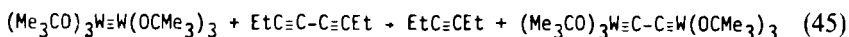
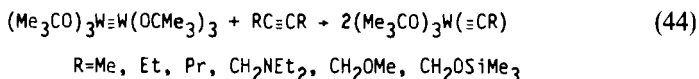


Green and co-workers reported an unusual 1,2-trimethylsilyl shift in the rearrangement of a metallacyclopropane to a carbyne complex [Eq. (43)] (111). The metallacyclopropane compound was structurally characterized by X-ray crystallography (111).

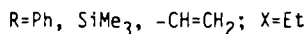
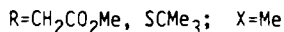
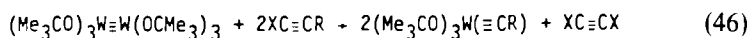


E. Metathesis of $\text{M}\equiv\text{M}$ Triple Bonds with Acetylenes and Nitriles

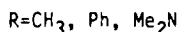
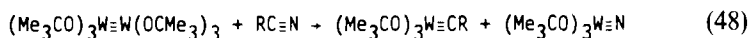
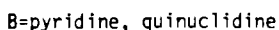
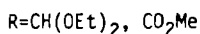
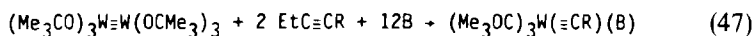
Metathesis of $\text{M}\equiv\text{M}$ triple bonds ($\text{M} = \text{Mo}, \text{W}$) with acetylenes and nitriles provides a valuable synthetic route to certain carbyne compounds. R. R. Schrock and co-workers reported that reactions of $(\text{Me}_3\text{CO})_3\text{W}\equiv\text{W}(\text{OCMe}_3)_3$ with symmetric acetylenes give the corresponding carbynes quantitatively [Eqs. (44) and (45)] (112,113). Similarly, asymmetric acetylenes react



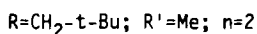
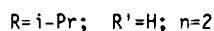
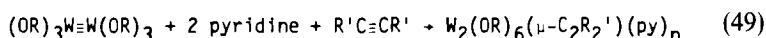
to give carbynes [Eq. (46)] (112,113); the end of the acetylene with the more electronegative substituent is found in the carbyne product. In some cases, the



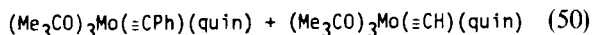
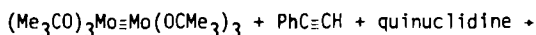
reactions occur only in the presence of bases [Eq. (47)] (113). The analogous reaction of $(\text{Me}_3\text{CO})_3\text{W}\equiv\text{W}(\text{OCMe}_3)_3$ with CH_3CN produces the carbyne as well as the nitrido compound [Eq. (48)] (59,112).



In contrast to Eqs. (44) and (45), $(\text{RO})_3\text{W}\equiv\text{W}(\text{OR})_3$ reacts with $\text{R}'\text{C}\equiv\text{CR}'$ ($\text{R}' = \text{Me}, \text{H}$) in the presence of pyridine to give alkyne adducts $\text{W}_2(\text{OR})_6(\mu\text{-C}_2\text{R}')(\text{py})_n$ according to Eq. (49) (70). Labeling studies, using

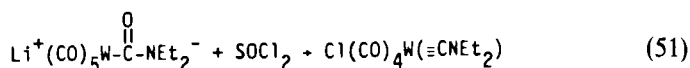


$\text{H}^{13}\text{C}^{13}\text{CH}$ and $\text{D}^{12}\text{C}^{12}\text{CD}$, suggest that the ethyne adduct $\text{W}_2(\text{O}-\text{t-Bu})_6(\mu\text{-C}_2\text{H}_2)(\text{py})$ is in equilibrium with $(\text{t-BuO})_3\text{W}(\equiv\text{CH})$. Metathesis of a $\text{Mo}\equiv\text{Mo}$ triple bond with $\text{PhC}\equiv\text{CH}$ has also been reported [Eq. (50)] (114).

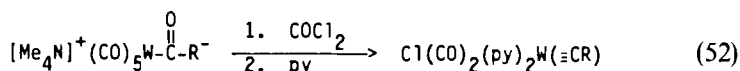


F. Oxygen Abstraction from $\text{M}-\text{C}(\text{O})\text{R}$ and $\text{M}-\text{C}(\text{O})\text{NR}_2$ Complexes

Fischer and Himmelreich reported the abstraction of oxygen from an anionic carbamoyl compound with SOCl_2 to give an aminocarbyne compound [Eq. (51)] (115). Similarly, oxygen abstraction from an anionic acyl complex

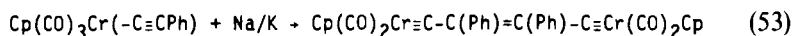


yields the corresponding carbyne compound [Eq. (52)] (116); COCl_2 , $\text{XC}(\text{O})\text{C}(\text{O})\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$), $\text{ClCO}_2\text{CCl}_3$, and $(\text{CF}_3\text{CO})_2\text{O}$ have been used in this type of reaction.

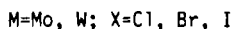
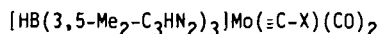
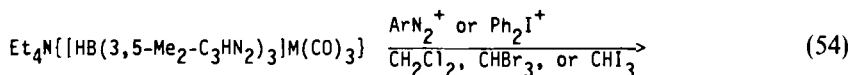


G. Miscellaneous Syntheses

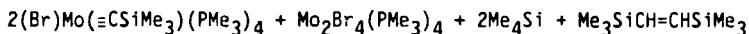
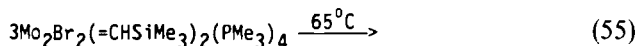
A number of other routes to carbynes, which fall outside the scope of the previously discussed methods, are described in this section. Reduction of $\text{Cp}(\text{CO})_3\text{Cr}(-\text{C}\equiv\text{CPh})$ with Na/K affords a dinuclear carbyne compound in approximately 20% yield [Eq. (53)] (33). The first halogenocarbyne com-



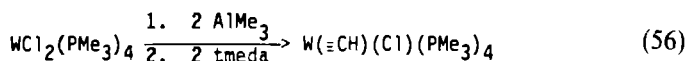
pound was prepared by oxidation of $[\text{HB}(3,5\text{-Me}_2\text{-C}_3\text{HN}_2)_3](\text{CO})_3\text{M}^-$ ($\text{M} = \text{Mo}, \text{W}$) with either ArN_2^+ ($\text{Ar} = \text{aryl}$) or Ph_2I^+ in the presence of a source of dihalogenoalkyl radicals [Eq. (54)] (44). A radical mechanism in-



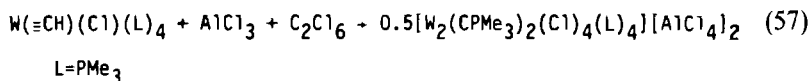
volving $[\text{HB}(3,5\text{-Me}_2\text{-C}_3\text{HN}_2)_3]\text{M}(\text{CO})_3\cdot$ and $\text{CHX}_2\cdot$ was proposed. A trimethylsilyl carbyne is formed by decomposition of $\text{Mo}_2\text{Br}_2(\equiv\text{CHSiMe}_3)_2(\text{PMe}_3)_4$ at 65°C [Eq. (55)] (40). This carbyne complex reacts with dppe ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) to give $(\text{Br})\text{Mo}(\equiv\text{CSiMe}_3)(\text{dppe})_2$ which was characterized by X-ray crystallography (40).



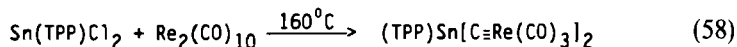
The first hydrido carbyne (methylidyne) compound was prepared in 60% yield by reaction of $\text{WCl}_2(\text{PMe}_3)_4$ with 2 equivalents of AlMe_3 followed by addition of tmeda ($\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$) [Eq. (56)] (117). An X-ray struc-



tural study of the product shows that the methylidyne and chloride ligands are trans to one another (62,116). The carbyne $\text{W}(\equiv\text{CH})(\text{Cl})(\text{PMe}_3)_4$ reacts with AlCl_3 in the presence of C_2Cl_6 to give a phosphinomethylidyne complex in 17% yield [Eq. (57)] (60). The molecule has a planar $\text{P}_2\text{W}(\mu\text{-Cl})_2\text{WP}_2$ framework with transoid CPMe_3 ligands (60).

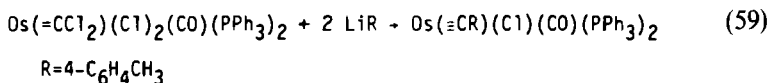


When $\text{Sn}(\text{TPP})\text{Cl}_2$ is heated with $\text{Re}_2(\text{CO})_{10}$ at 160°C , $(\text{TPP})\text{Sn}[\text{C}\equiv\text{Re}(\text{CO})_3]_2$ is formed [Eq. (58)] (118). X-Ray structural data show that the tin



$\text{TPP} = 5,10,15,20\text{-tetraphenylporphyrinato}$

and rhenium atoms are linked by a carbido carbon atom, which has a carbyne-like bond to the rhenium atom (118). The $\text{Re}\equiv\text{C}$ distance is 1.747 \AA , and the $\text{Sn}-\text{C}\equiv\text{Re}$ angle is $138.5(8)^\circ$. An osmium carbyne is prepared in 70% yield by reaction of $\text{Os}(=\text{CCl}_2)(\text{Cl})_2(\text{CO})(\text{PPh}_3)_2$ with 2 equivalents of LiR ($\text{R} = 4\text{-C}_6\text{H}_4\text{CH}_3$) [Eq. (59)] (67). An X-ray structural determination of the



product shows distorted trigonal bipyramidal geometry around the Os with the phosphine ligands mutually trans, and the $\text{Os}\equiv\text{C}$ stretching frequency is observed at 1374 cm^{-1} (67).

IV

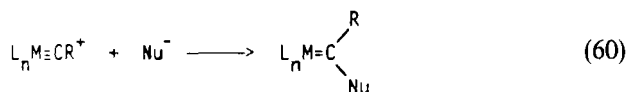
REACTIONS OF CARBYNE LIGANDS

A. Reactions of Carbyne Complexes with Nucleophiles

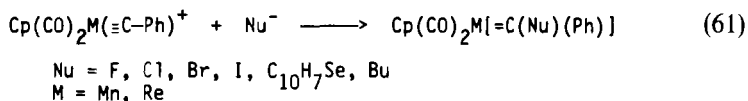
Numerous reactions of carbyne compounds with nucleophiles have been studied (2). These reactions proceed either by nucleophilic addition to the carbyne carbon atom or by substitution of other ligands bound to the metal. The discussion here is based mainly on studies of E. O. Fischer and co-workers.

1. Nucleophilic Addition to Carbyne Carbon

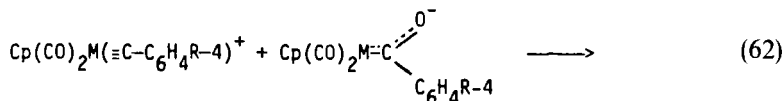
Reactions of cationic carbyne compounds with nucleophiles proceed exclusively by nucleophilic attack at the carbyne carbon atom, thus providing a synthetically useful route to certain carbene complexes [Eq. (60)]. It has been proposed that this attack is frontier orbital controlled (14-16; see Section II,A).



H. Fischer (2) reviewed these types of reactions up to 1982 involving the cationic carbynes $(CO)_5Cr(\equiv CNR_2)^+$, $Cp(CO)_2M(\equiv C-Ph)^+$ ($M = Mn, Re$), $Cp(CO)_2Re(\equiv C-SiPh_3)^+$, and $(\eta^6-C_6H_{6-n}Me_n)(CO)_2Cr(\equiv C-Ph)^+$ ($n = 0, 1, 2, 3$) with various nucleophiles. More recent examples of nucleophilic addition are the reactions of $Cp(CO)_2M(\equiv C-Ph)^+$ ($M = Mn, Re$) with F^- (119), Cl^- (119), Br^- (119), I^- (119), $C_{10}H_7Se^-$ (120), and Bu^- (120) to give the corresponding neutral carbene compounds [Eq. (61)]. The $(\eta^5-C_5H_4Me)(CO)_2Mn(\equiv C-fc)^+$ (fc = ferrocenyl) carbyne reacts with XPh^- ($X = S, Se, Te$) (121) and $Co(CO)_4^-$ (122) to produce the corresponding ferrocenyl carbene compounds.

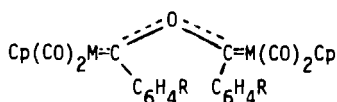


The rhenium carbyne compounds, $Cp(CO)_2Re(\equiv C-SiPh_3)^+$ (123) and $(CO)_5Re-Re(CO)_4(\equiv C-SiPh_3)^+$ (123,124), react with $HOEt$ and $HNMe_2$ to give the corresponding alkoxy and amino carbene compounds, respectively. An interesting symmetric carbene anhydride can be prepared by reaction of $Cp(CO)_2M(\equiv C-C_6H_4R)^+$ and $Cp(CO)_2M[-C(=O)C_6H_4R]^-$ [Eq. (62)] (125). Reaction of $(CO)_5Cr(\equiv CNET_2)^+$ with N_3^- produces



$M = Mn, Re$

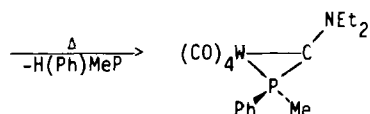
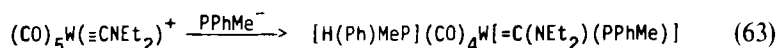
$R = H, CF_3$



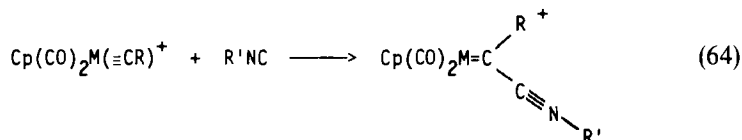
$(CO)_5Cr(N \equiv C-NEt_2)$, which was suggested to form via the intermediate $(CO)_5Cr[=C(N_3)(NEt_2)]$ by loss of N_2 and rearrangement to the product

(126). The structure of the product was determined by X-ray crystallography (126).

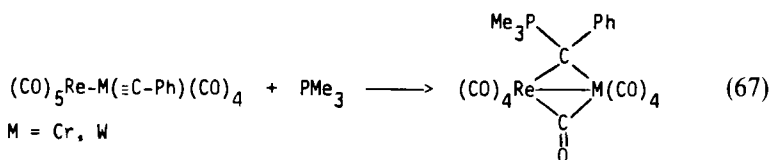
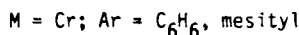
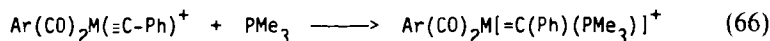
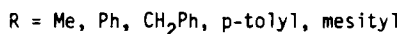
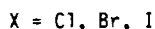
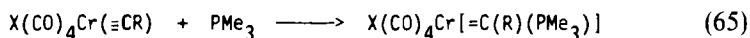
The tungsten carbyne compound $(\text{CO})_5\text{W}(\equiv\text{CNEt}_2)^+$ reacts with $\text{K}[\text{P}(\text{Me})\text{Ph}]$ in THF, yielding among other products a carbene complex, which on thermolysis eliminates the trans phosphine ligand to give a metallacyclic carbene complex [Eq. (63)] (127,128).



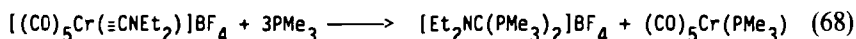
Beside the aforementioned anionic nucleophiles, neutral nucleophiles such as phosphines and isocyanides can also add to the carbyne carbon. Thus, $\text{Cp}(\text{CO})_2\text{M}(\equiv\text{C}-\text{R})^+$ ($\text{M} = \text{Mn}, \text{Re}$; $\text{R} = \text{Ph}, \text{Me}$) reacts with isocyanides $\text{R}'\text{NC}$ ($\text{R}' = \text{Me}, \text{cyclohexyl}, \text{tert-butyl}$) to give keteneiminyll compounds [Eq. (64)] (129,130). Similarly, phosphines add to carbyne carbons to give



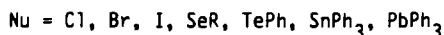
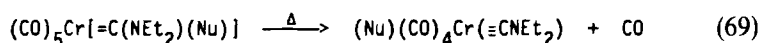
ylides [Eqs. (65) and (66)] (131-133). Bridging ylides can be obtained by reaction of dinuclear carbynes with PMe_3 [Eq. (67)] (134). A novel ylide is



liberated from $(\text{CO})_5\text{Cr}(\equiv\text{CNEt}_2)^+$ upon reaction with PMe_3 [Eq. (68)] (135,136).



As mentioned earlier, $(\text{CO})_5\text{Cr}(\equiv\text{CNEt}_2)^+$ reacts with a great number of different nucleophiles to give neutral carbene compounds (2). When these carbene compounds are heated, the Nu group often migrates from the carbon to the metal center [Eq. (69)] (137,138); kinetic investigations indicate that this



rearrangement follows a first-order rate law (36,84,139–143). External CO pressure (up to 100 atm), radical initiators [azobis(isobutyronitrile)], radical inhibitors (hydroquinone), and free Nu^- ions do not influence the reaction rate. Therefore, an intramolecular mechanism involving migration of Nu onto the metal center with simultaneous expulsion of a CO ligand has been proposed (36,84,139–143). The rate of the rearrangement is determined mainly by the bulk of the amino substituent NR_2 . The diethylaminocarbene complex rearranges 16 times faster and the diphenylaminocarbene complex rearranges 100 times faster than the dimethylaminocarbene derivative (84,139). However, the effect of different Nu migrating groups is very small, and no obvious trends are evident (139). When Nu is F, SiPh_3 , OEt, NCS, NCO, and CN, however, no rearrangement according to Eq. (69) is observed (138).

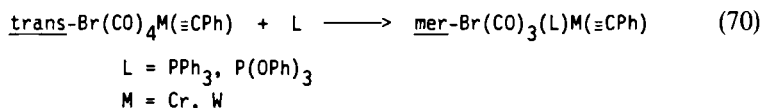
Reactions of the molybdenum (42) and tungsten (58,144) aminocarbene compounds $(\text{CO})_5\text{M}(\equiv\text{CNEt}_2)^+$ ($\text{M} = \text{Mo}, \text{W}$) with halides and selenides immediately yield the corresponding neutral carbyne complexes $(\text{Nu})(\text{CO})_4\text{M}(\equiv\text{CNEt}_2)$ ($\text{M} = \text{Mo}, \text{W}$; $\text{Nu} = \text{Br}, \text{I}, \text{SeR}$); no carbene intermediates were detected. Only AsPh_2^- and $\text{Se}(4\text{-C}_6\text{H}_4\text{CF}_3)^-$ add to the carbene carbon in $(\text{CO})_5\text{W}(\equiv\text{CNEt}_2)^+$ to give $(\text{CO})_5\text{W}[\text{C}(\text{NEt}_2)(\text{Nu})]$ [$\text{Nu} = \text{AsPh}_2, \text{Se}(4\text{-C}_6\text{H}_4\text{CF}_3)$] (58,144). These nucleophiles do not migrate to the W to give *trans*-(Nu)(CO)₄W(≡CNEt₂) on heating in solution (58,144).

2. Substitution of Other Ligands

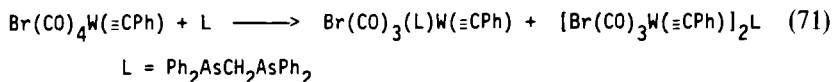
Cationic carbyne compounds undergo attack by nucleophiles exclusively at the carbyne carbon atom. On the other hand, neutral carbyne complexes show very different reactivities toward nucleophiles. Depending on the nucleophilicity of the reactant, these carbynes may undergo attack at the carbyne carbon atom or substitution of a CO or the trans-positioned halide ligand. The difference in reactivity of cationic and neutral carbyne complexes has

been explained theoretically (15). The maximum coefficient in the LUMO is at the carbyne carbon atom in the cationic carbyne complex, $(\text{CO})_5\text{Cr}(\equiv\text{CH})^+$, but at the Cr atom in the neutral $\text{Cl}(\text{CO})_4\text{Cr}(\equiv\text{CH})$ (15). However, for $\text{Cl}(\text{CO})_4\text{Cr}(\equiv\text{CH})$, the LUMO and the next higher LUMO, whose maximum coefficient is at the carbyne carbon, are very close energetically. Thus, one can understand the nature of the observed products for both cationic and neutral carbyne complexes using frontier orbital theory (15). When the nucleophilic reagent is strong, it attacks both the Cr and the carbyne carbon atom because of the very small energy separation between the LUMO and the next higher LUMO. On the other hand, a weak nucleophile would attack only the Cr atom where the LUMO has the maximum coefficient.

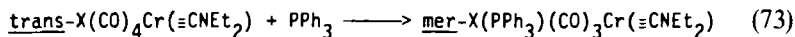
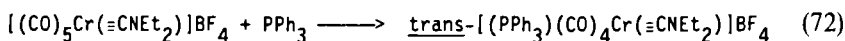
As mentioned earlier, trimethylphosphine and isocyanides can add to the carbyne carbon atom [Eqs. (64)–(66)]. However, substitution of CO ligands in carbyne compounds can also occur. Thus, PPh_3 and $\text{P}(\text{OPh})_3$ substitute a CO ligand in *trans*- $\text{Br}(\text{CO})_4\text{M}(\equiv\text{CPh})$ [Eq. (70)] (131). Substitution of



two CO ligands in *trans*- $\text{Br}(\text{CO})_4\text{M}(\equiv\text{CPh})$ ($\text{M} = \text{Cr}, \text{W}$) is possible with pyridine, PPh_3 , *t*-BuNC, and $\text{P}(\text{OPh})_3$ (131). Bidentate ligands (2,2'-bipyridine and 1,10-phenanthroline) substitute two CO ligands in *trans*- $\text{Br}(\text{CO})_4\text{M}(\equiv\text{CR})$ ($\text{M} = \text{Cr}, \text{W}, \text{R} = \text{Me}, \text{Ph}; \text{M} = \text{Mo}, \text{R} = \text{Ph}$) (145). The bidentate ligand $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$ can add to one or two metal centers [Eq. (71)] (146).

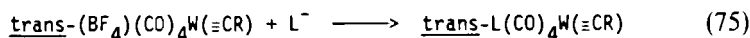
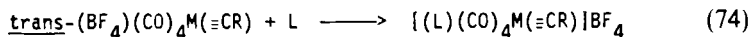


Similarly, aminocarbyne compounds undergo substitution of CO by PPh_3 [Eqs. (72) and (73)] (37). These reactions follow a first-order rate law in the presence of excess PPh_3 which together with the activation parameters ($\Delta H^\ddagger = 104\text{--}113\text{ kJ mol}^{-1}$, $\Delta S^\ddagger = 64\text{--}71\text{ J mol}^{-1}\text{ K}^{-1}$) indicates a mechanism involving rate-determining CO dissociation. The reaction in Eq. (72) ($k^{25^\circ\text{C}} = 10.3 \times 10^{-3}\text{ second}^{-1}$) takes place twice as fast as the reaction of *trans*- $\text{Br}(\text{CO})_4\text{Cr}(\equiv\text{CNEt}_2)$ [Eq. (73)] ($k^{25^\circ\text{C}} = 5.39 \times 10^{-3}\text{ second}^{-1}$) and 30 times

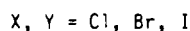
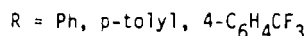
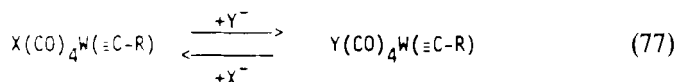
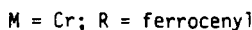
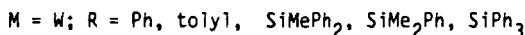
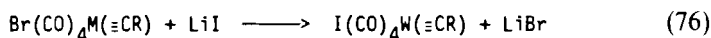


as fast as reaction of *trans*-I(CO)₄Cr(≡CNEt₂) [Eq. (73)] ($k^{25^\circ\text{C}} = 0.358 \times 10^{-3} \text{ second}^{-1}$) (147).

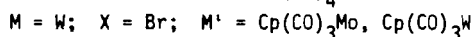
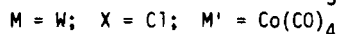
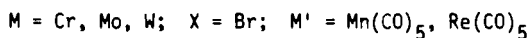
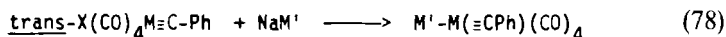
The weakly coordinated BF₄ is labile and can be substituted by neutral or anionic nucleophiles [Eqs. (74) and (75)] (148,149). Related to the above substitution reactions is the halide exchange of *trans*-X(CO)₄M(≡CR). The



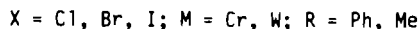
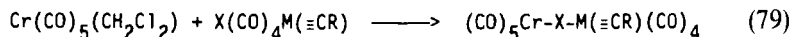
trans Br⁻ ligand can be substituted by I⁻ [Eq. (76)] (31,150,151). Similarly, X(CO)₄W(≡CR) exchanges its halide ligand reversibly [Eq. (77)] (152,153).



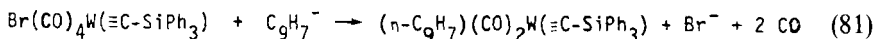
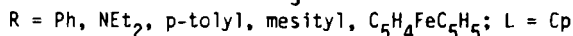
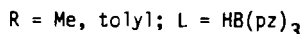
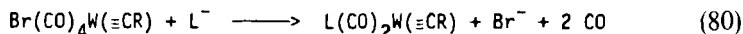
This substitution reaction follows a second-order rate law, first order each in the concentrations of X(CO)₄W(≡CPh) and Y⁻ (152). Activation parameters for the replacement of I⁻ by Br⁻ in 1,1,2-trichloroethane are $\Delta H^\ddagger = 56.7 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -33 \text{ J mol}^{-1} \text{ K}^{-1}$ (152). Coordinated iodide (X = I; R = Ph) is substituted more than three times faster by chloride than by bromide. The influence of the leaving halide is relatively small: $k(\text{Br})/k(\text{I}) = 1.2$ (Y = Cl) (152). These kinetic results support an associative mechanism. Nucleophilic attack at the carbyne carbon is suggested as the rate-determining step (152). Substitution of the halide ion in X(CO)₄M(≡CR) with metal anions provides a route to bimetallic carbyne compounds [Eq. (78)] (41,52,150).



Similarly, substitution of Br^- in $\text{trans-Br}(\text{CO})_4\text{W}(\equiv\text{CR})$ ($\text{R} = \text{SiPh}_3, \text{C}_{10}\text{H}_{19}$) by $\text{Re}(\text{CO})_5^-$ occurs to give $(\text{CO})_5\text{ReW}(\equiv\text{CR})(\text{CO})_4$ (26,151). Addition of $\text{X}(\text{CO})_4\text{M}(\equiv\text{CR})$ to $\text{Cr}(\text{CO})_5(\text{CH}_2\text{Cl}_2)$, which is generated by irradiation of $\text{Cr}(\text{CO})_6$ in CH_2Cl_2 at -30°C , produces halo-bridged dinuclear carbyne compounds [Eq. (79)] (154).

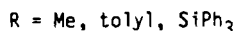
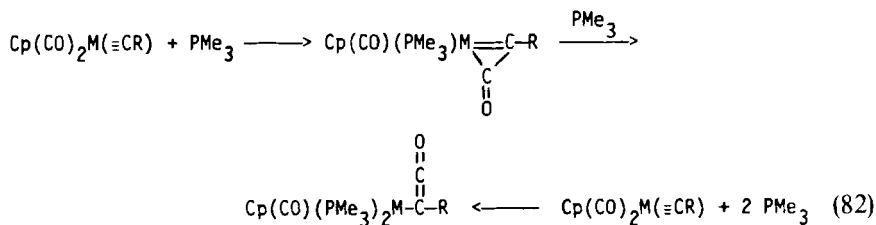


Cyclopentadienide (Cp^-), $\text{HB}(\text{pz})_3^-$, and indenide (C_9H_7^-) displace two CO and one halide ligand in $\text{Br}(\text{CO})_4\text{W}(\equiv\text{CR})$ according to Eqs. (80) and (81) (54,55,151,155); in contrast, Cp^- adds to the carbyne carbon in $\text{Cp}(\text{CO})_2\text{-Mn}(\equiv\text{CMe})^+$ (156). The analogous carbaborane complex $\text{W}[\equiv\text{C}-(\text{tolyl})](\text{CO})_2(\eta\text{-}1,2\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)^-$ can be prepared by reaction of $\text{Br}(\text{CO})_4\text{W}[\equiv\text{C}-(\text{tolyl})]$ with $\text{Na}_2[7,8\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2]$ (157).

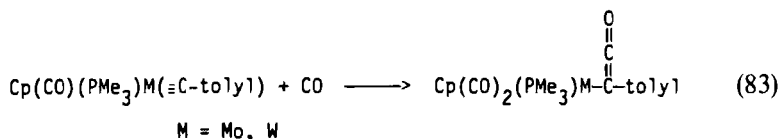


3. Formation of Ketenyl Compounds

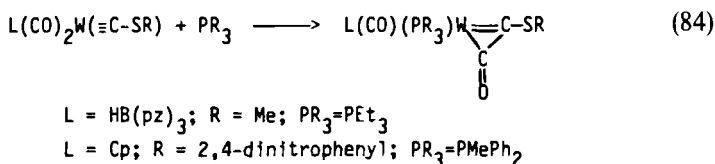
In the above two subsections, carbynes reacted with phosphines to give ylides or substituted products. Quite another type of reaction occurs in electron-rich complexes where the carbyne ligand is not susceptible to nucleophilic attack; in these cases, PMe_3 causes carbonylation of the carbyne to give η^1 - or η^2 -ketenyl compounds. Thus, reaction of $\text{Cp}(\text{CO})_2\text{M}(\equiv\text{CR})$ ($\text{M} = \text{Mo}, \text{W}; \text{R} = \text{Me}, \text{tolyl}$) with 1 equivalent of PMe_3 produces η^2 -ketenyl compounds [Eq. (82)] (158,159). Addition of another mole of PMe_3 to the η^2 -ketenyl compound or addition of 2 mol of PMe_3 directly to the carbyne gives η^1 -ketenyl



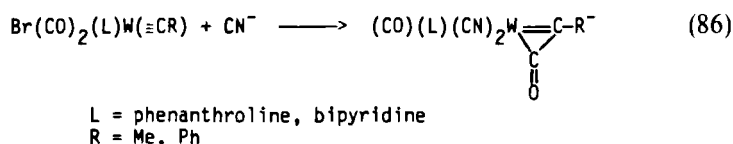
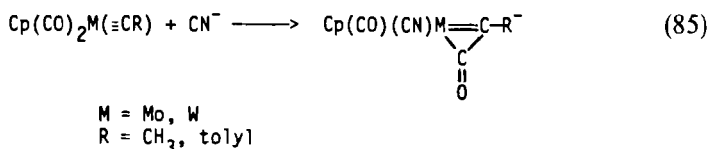
compounds [Eq. (82)] (159,160). Bidentate phosphine ligands, $\text{Me}_2\text{P}(\text{CH}_2)_n\text{PMe}_2$ ($n = 1$ or 2) and $(\text{PF}_2)_2\text{NCH}_3$, also react with $\text{Cp}(\text{CO})_2\text{W}[\equiv\text{C}-(\text{tolyl})]$ to give the corresponding η^1 -ketenyl compounds (161). Interestingly, direct carbonylation of $\text{Cp}(\text{PMe}_3)(\text{CO})\text{M}[\equiv\text{C}-(\text{tolyl})]$ also yields an η^2 -ketenyl compound [Eq. (83)] (162).



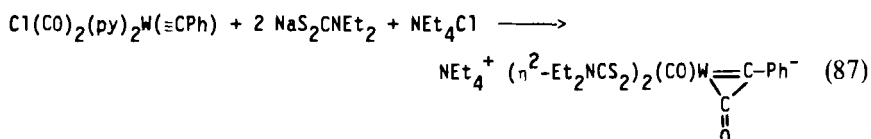
The thiocarbene compounds, $[\text{HB}(\text{pz})_3](\text{CO})_2\text{W}(\equiv\text{CSMe})$ and $\text{Cp}(\text{CO})_2\text{W}(\equiv\text{C}-\text{S}-\text{DNP})$ ($\text{DNP} = 2,4\text{-dinitrophenyl}$), react similarly with PEt_3 and PMePh_2 , respectively, to give η^2 -ketenyl compounds [Eq. (84)] (163).



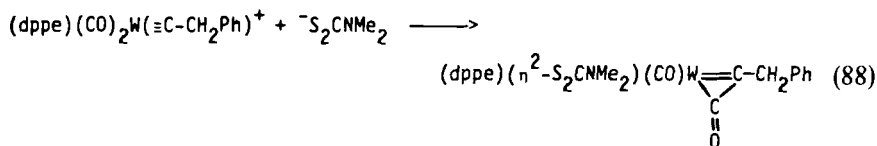
Anionic η^2 -ketenyl compounds are formed in reactions of carbyne compounds $\text{Cp}(\text{CO})_2\text{M}(\equiv\text{CR})$ (164) and $\text{Br}(\text{CO})_2(\text{L})\text{W}(\equiv\text{CR})$ (165,166), with CN^- [Eqs. (85) and (86)]. Similarly, $\text{Cl}(\text{CO})_2(\text{py})_2\text{W}(\equiv\text{CPh})$ reacts with 2



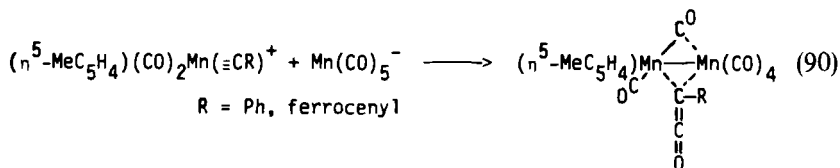
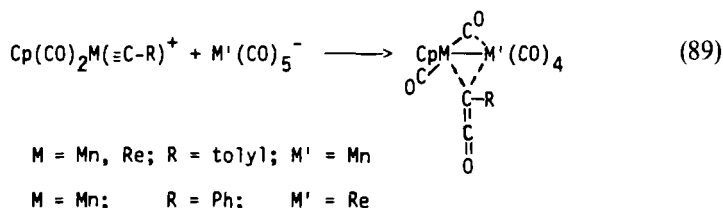
equivalents of sodium diethyldithiocarbamate, $\text{NaS}_2\text{CNET}_2$, to give an anionic phenylketenyl compound [Eq. (87)] (167). Loss of CO from $[\text{mer}(\text{dppe})(\text{CO})_3\text{W}(\equiv\text{C}-\text{CH}_2\text{Ph})][\text{BF}_4]$ occurs in refluxing CH_2Cl_2 to form



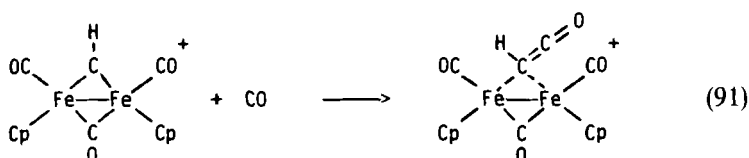
$[(dppe)(CO)_2W(\equiv C-CH_2Ph)][BF_4]$ (110). Reaction of the cationic carbyne $(dppe)(CO)_2W(\equiv C-CH_2Ph)^+$ with $^-S_2CNMe_2$ produces a neutral ketenyl compound [Eq. (88)] (110).



Unusual bridging ketenyl compounds are formed in reactions of cationic carbyne complexes with $Mn(CO)_5^-$ and $Re(CO)_5^-$ [Eqs. (89) and (90)]



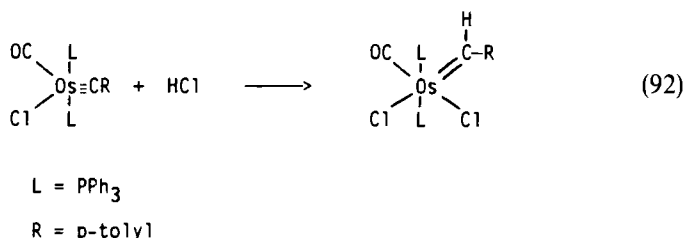
(122,168,169); in contrast, reactions of $(\eta^5-MeC_5H_4)(CO)_2Mn(\equiv CR)^+$ ($R = Ph$ or ferrocenyl) with $Co(CO)_4^-$ produce the neutral carbene compounds $(\eta^5-MeC_5H_4)(CO)_2Mn\{\equiv C(R)[Co(CO)_4]\}$ (122). These bridging ketenyl compounds are postulated to form via CO transfer in the carbene intermediate (122). X-Ray structural studies of the bridging ketenyl compounds $Cp(CO)_2Mn[\mu-C(CO)-\text{tolyl}]Mn(CO)_4$ (168), $(\eta^5-MeC_5H_4)(CO)_2Mn[\mu-C(CO)-\text{ferrocenyl}]Mn(CO)_4$ (122), and $Cp(CO)_2Mn[\mu-C(CO)-Ph]Re(CO)_4$ (169) show common structural features: the $M-M'$ bond is bridged by the α -carbon atom of the ketenyl ligands and semibridged by a CO group. The bridging ketenyl is best represented by a two-electron, three-center bonding scheme (170). A bridging ketenyl compound has also been prepared by carbonylation of the bridging carbyne ligand in $Cp(CO)Fe(\mu-CH)(\mu-CO)Fe(CO)Cp^+$ [Eq. (91)] (170).



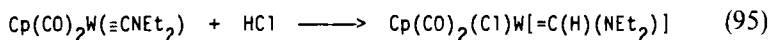
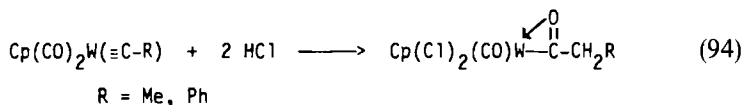
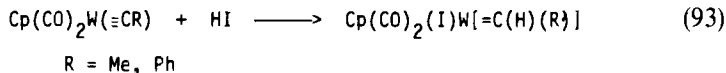
B. Reactions of Carbyne Complexes with Electrophiles

1. Reactions with Protonic Acids

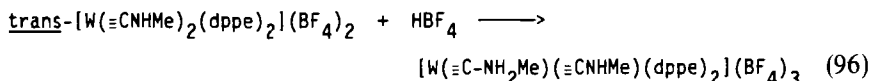
The addition of H^+ to electron-rich carbyne ligands yields hydridocarbene compounds. The protonation of $(Cl)(CO)(PPh_3)_2Os[\equiv C-(tolyl)]$ with HCl produces a neutral carbene compound [Eq. (92)] (67). Similarly, reactions of $Cp(CO)_2W(\equiv CR)$ ($R = Me, tolyl$) with HI give neutral carbenes



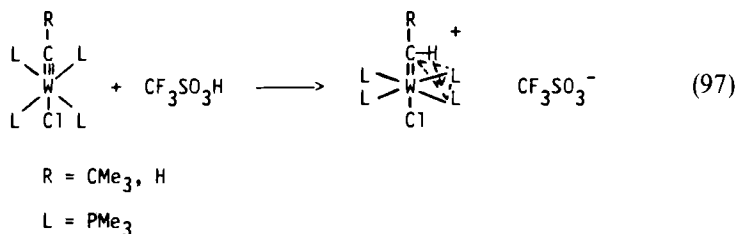
[Eq. (93)] (171). However, reactions of the same carbyne compounds with 2 equivalents of HCl yield η^2 -acyl compounds [Eq. (94)] (172). The protonation of an aminocarbyne compound [Eq. (95)] with HCl produces a neutral



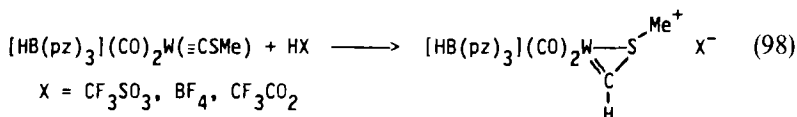
aminocarbene (173). In contrast, protonation of the nitrogen occurred in the reaction of the dicationic aminocarbyne compound *trans*- $[W(\equiv CNHMe)_2(dppe)_2]^{2+}$ with H^+ [Eq. (96)] (100).



Protonation of carbynes with acids of weakly coordinating anions ($CF_3SO_3^-$ or BF_4^-) gives cationic hydridocarbenes; for example, protonation of $W(\equiv CR)(PMe_3)_4(Cl)$ ($R = CMe_3, H$) with CF_3SO_3H yields grossly distorted carbene compounds [Eq. (97)], in which the α -hydrogen atom is proposed to migrate around the C_2L_2 face of the octahedron (174,175). The proposal is

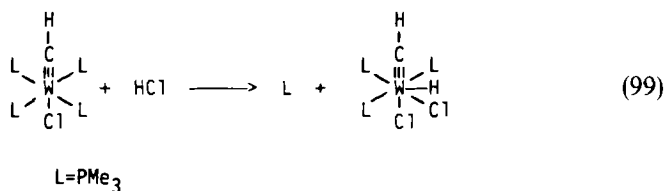


supported by the signal for the α proton ($\text{R} = \text{CMe}_3$), which is found at -8.3 ppm as a quintet ($J_{\text{HP}} = 8.8$ Hz), and the ^{13}C -NMR spectrum shows a doublet resonance at 241.9 ppm with a J_{CH} of 45 Hz (174,175). Protonation of the thiocarbonyl complex $[\text{HB}(\text{pz})_3](\text{CO})_2\text{W}(\equiv\text{CSMe})$ with HX ($\text{X} = \text{CF}_3\text{SO}_3, \text{BF}_4, \text{CF}_3\text{CO}_2$) produces an η^2 -thiocarbene compound, where the carbene ligand $[\text{CH}(\text{SMe})]$ bonds to tungsten through both the carbon and sulfur atoms [Eq. (98)] (11).

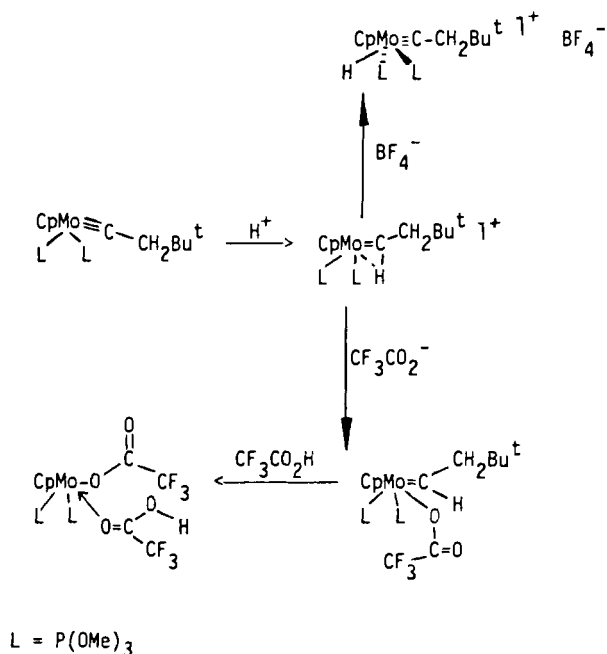


Reactions of $\text{Cp}[\text{P}(\text{OMe})_3]_2\text{Mo}(\equiv\text{C}-\text{CH}_2\text{Bu}^t)$ with HBF_4 and $\text{CF}_3\text{CO}_2\text{H}$ yield two different products, depending on the coordinating abilities of the anions (BF_4^- or CF_3CO_2^-) (19). With HBF_4 , the hydride compound is the final compound (Scheme 2), whereas the reaction of 2 equivalents of $\text{CF}_3\text{CO}_2\text{H}$ results in cleavage of the carbyne fragment from the metal to yield $\text{Cp}[\text{P}(\text{OMe})_3]_2\text{Mo}(\text{O}_2\text{CCF}_3)(\text{CF}_3\text{CO}_2\text{H})$ (Scheme 2) (19). It was proposed that the proton initially adds to the carbyne carbon, although there was no direct evidence for it. Other reactions described in this section, however, clearly support such a protonated-carbyne intermediate.

Protonation at the metal center is observed in the reaction of $\text{W}(\equiv\text{CH})(\text{PMe}_3)_4(\text{Cl})$ [Eq. (99)] (174,175). Analogous bidentate phosphine

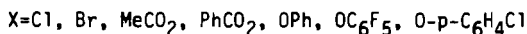
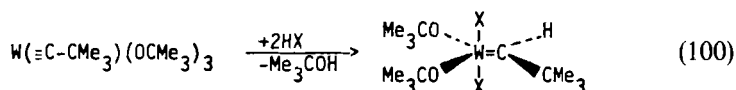


compounds $\text{W}(\equiv\text{CR})(\text{dmpe})_2(\text{Cl})$ ($\text{R} = \text{CMe}_3, \text{H}$) also undergo protonation at the metal center with HCl , as well as with $\text{CF}_3\text{SO}_3\text{H}$, to give $[\text{W}(\equiv\text{CR})(\text{dmpe})_2(\text{H})(\text{Cl})]\text{X}$ ($\text{X} = \text{Cl}, \text{CF}_3\text{SO}_3$) (174,175). Protonation of $\text{W}(\equiv\text{CCMe}_3)(\text{OCMe}_3)_3$ with 2 equivalents of various acids gives the

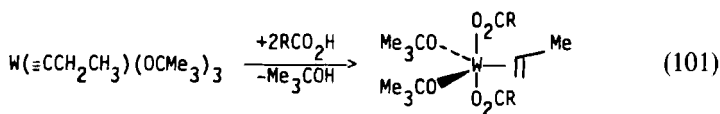


SCHEME 2

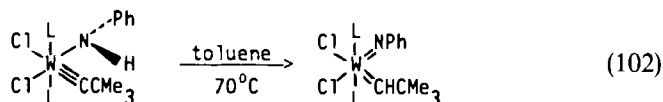
hydridocarbene product [Eq. (100)] (176). Related to the above protonation is the reaction of $\text{W}(\equiv\text{CR})(\text{OCMe}_3)_3$ ($\text{R} = \text{Me}, \text{Et}$) with 1 equivalent of $\text{CH}_3\text{CO}_2\text{H}$ to give $\text{W}(\equiv\text{CHR})(\text{OCMe}_3)_3(\text{O}_2\text{CCH}_3)$ (176). Addition of 2 or



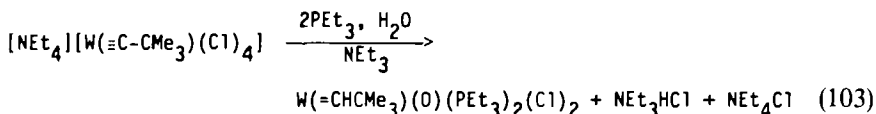
more equivalents of RCO_2H to $\text{W}(\equiv\text{CCH}_2\text{CH}_3)(\text{OCMe}_3)_3$, however, yields a propylene compound [Eq. (101)] (176). It is proposed that this reaction occurs by double protonation of the propylidyne complex to give a propyl intermediate, which subsequently loses a proton from the β -carbon to give the propylene compound.



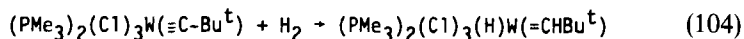
Proton transfer from the amido ligand to the carbyne carbon occurs during the thermolysis of $W(\equiv C-CMe_3)(Cl)_2(PEt_3)_2(NHPh)$ [Eq. (102)]



(48). Water is the proton source (177) in the formation of a hydridocarbene complex from the reaction of $W(\equiv C-CMe_3)(Cl)_4^-$ with H_2O in the presence of PEt_3 and NEt_3 [Eq. (103)] (48). A related conversion of a

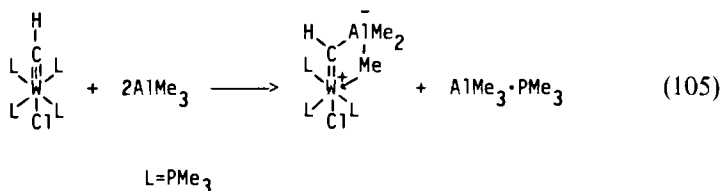


carbyne to a hydridocarbene ligand occurs in the reaction of $(PMe_3)_2(Cl)_3W(\equiv C-CMe_3)$ with H_2 , where addition of H_2 across the $W \equiv C$ triple bond gives the hydridocarbene compound [Eq. (104)] (88).

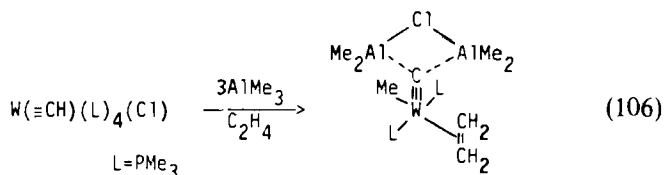


2. Reactions with Lewis Acids

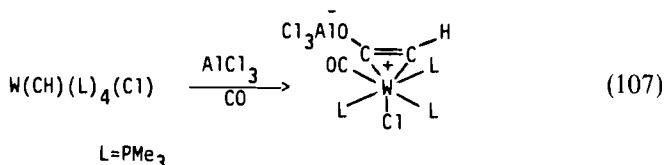
Besides H^+ , other Lewis acids add to the carbon atom of carbyne ligands. The carbyne compound $W(\equiv CH)(PMe_3)_4Cl$ reacts with H^+ [Eq. (97)] (174,175) as well as with $AlMe_3$ [Eq. (105)] (60,117); the $AlMe_3$ adds to



the carbyne carbon, and the structure of the product was determined by X-ray crystallography (62). In the presence of ethylene, however, $W(\equiv CH)(PMe_3)_4(Cl)$ reacts differently with $AlMe_3$. The methylidyne proton is lost, and a dialuminated methylidyne complex is formed [Eq. (106)] (60,178).

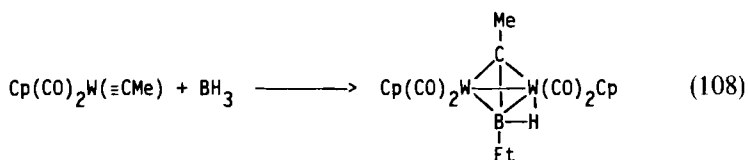


The $W(\equiv CH)(L)_4(Cl)$ complex reacts with CO and $AlCl_3$ to yield the product $W(HC\equiv COAlCl_3)(CO)(PMe_3)_3Cl$ in which the methylidyne ligand and CO have coupled to form an acetylene-type ligand, as revealed by an X-ray structural study (C—C bond length = 1.316 Å) [Eq. (107)] (60,179,180). This

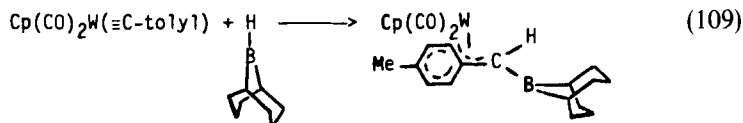


coupling of CO and methylidyne is similar to the aforementioned carbonylation of carbyne to give ketenyl compounds [Eqs. (82)–(88)]. $AlCl_3$ may not be involved directly in the coupling reaction; its primary role may simply be to labilize one of the PMe_3 ligands in $W(\equiv CH)(PMe_3)_4(Cl)$ or to stabilize the product.

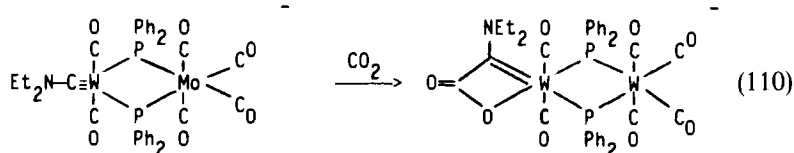
Reaction of $Cp(CO)_2W(\equiv CMe)$ with BH_3 gives a remarkable dinuclear boron compound in 70% yield [Eq. (108)] (181); the ethyl group attached to



the boron atom in the product must result from cleavage of a $W\equiv C$ bond, and all three hydrogens of the BH_3 group are incorporated into the final product. Two of the hydrogens have been transferred to a carbyne carbon atom, while the third forms a $B(\mu-H)W$ bridge (181). In contrast, the hydroborating reagent 9-borabicyclo[3.3.1]nonane (9-BBN), with only one active B—H bond per molecule, reacts with a similar carbyne compound to give a hydride addition product [Eq. (109)] (181). Carbon dioxide also acts as a Lewis acid in



adding across the $W\equiv C$ bond in $(Et_2NC\equiv)W(CO)_2(\mu-PPh_2)Mo(CO)_4^-$ according to Eq. (110) (182).

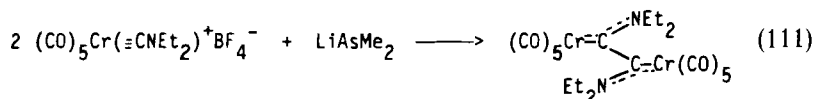


C. Coupling of Carbyne Ligands

Hoffmann and co-workers (183) examined theoretically the coupling of methyne ligands on one and two metal centers using the extended Hückel method. According to the calculation, coupling of bis(methynes) on one metal center $[L_nM(\equiv CH)_2]$ to give acetylenes $[L_nM(HC\equiv CH)]$ is allowed in d^2 and d^4 metal systems. For d^6 and higher systems, however, coupling is forbidden. Coupling of bis bridging methynes $[L_nM(\mu-CH)_2ML_n]$ to give μ -acetylene $[L_nM(\mu-HC\equiv CH)ML_n]$ is allowed for electron counts of $d^{12}-d^{12}$ and $d^{10}-d^{10}$. For d^8-d^8 systems, the bis bridging methyne lies 1 eV above the acetylene complex with no barrier to their interconversion. Experimentally, carbyne ligands can be induced to couple by three different methods.

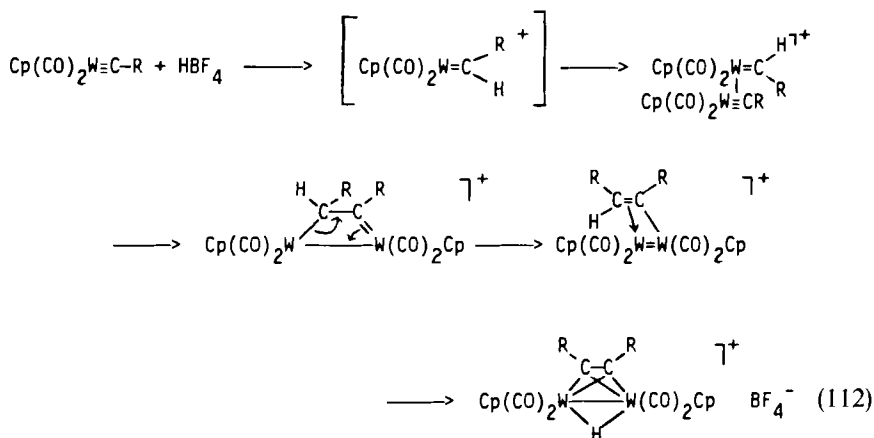
1. Reductive Coupling

Reaction of $(CO)_5Cr(\equiv CNEt_2)^+BF_4^-$ with $LiAsMe_2$ leads to a dimeric carbene complex by reductive coupling of the two carbyne fragments [Eq. (111)] (184). Coupling of $(CO)_5W(\equiv CNEt_2)^+$ is observed with PPh_2^- , PEt_2^- , $PMPh^-$, $SbPh_2^-$, and $BiPh_2^-$ (185), whereas NPh_2^- (185) and $AsPh_2^-$ (58) add to the carbyne carbon to give monomeric carbene complexes as shown in Eq. (60).



2. H^+ -Induced Coupling

Reaction of $Cp(CO)_2W(\equiv CR)$ ($R = Me$ or $4-C_6H_4Me$) with HBf_4 produces the hydrido- and alkyne-bridged ditungsten complexes [Eq. (112)]

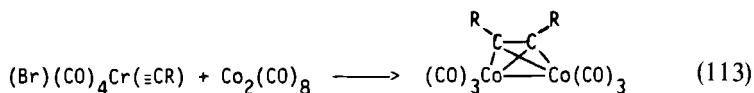


(171,186). Even though there is no direct evidence for any of the proposed intermediates shown in Eq. (112), it seems probable that the hydridocarbene resulting from protonation of the carbyne C is involved. In contrast to this reaction, $\text{Cp}(\text{CO})_2\text{W}(\equiv\text{CR})$ reacts with HI to give $\text{Cp}(\text{CO})_2\text{W}(=\text{CHR})(\text{I})$ [Eq. (93)] (171).

3. Coupling of Terminal Carbynes on Two or Three Metal Centers

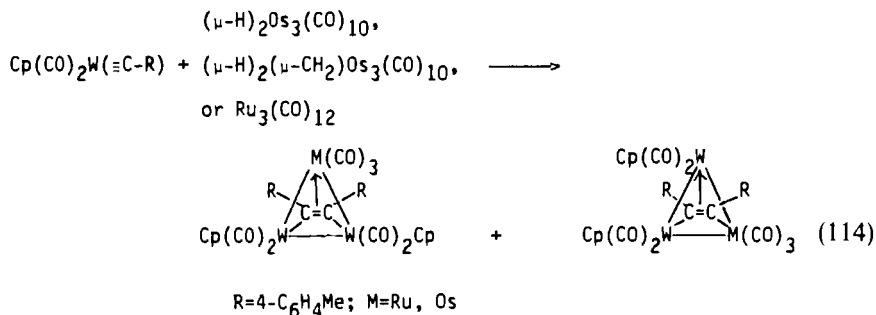
As mentioned earlier, coupling of bis- μ -alkylidyne ligands to give μ -acetylene is allowed theoretically (183). Formation of μ -alkynes from bis- μ -alkylidyne ligands is indeed observed (187,188). Reversible μ -alkyne scission/ μ -alkylidyne coupling has also been observed (70,188). However, we limit our discussion only to the coupling of terminal carbynes.

The carbyne ligands in $(\text{Br})(\text{CO})_4\text{M}(\equiv\text{CR})$ ($\text{R} = \text{Me}, \text{Ph}$; $\text{M} = \text{W}, \text{Cr}$), $(\text{Cl})(\text{CO})_4\text{Mo}(\equiv\text{C}-\text{tolyl})$, and $\text{Cp}(\text{CO})_2\text{Mn}(\equiv\text{CPh})^+$ couple under very mild conditions in the presence of $\text{Co}_2(\text{CO})_8$ to give μ -alkyne dicobalt complexes [Eq. (113)] (189). Similarly, $(\text{Br})(\text{CO})_4\text{Cr}(\equiv\text{CPh})$ reacts with

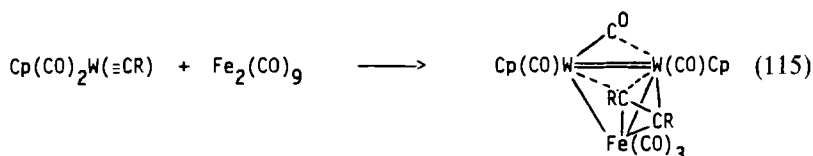


Cp_2Ni to give $\text{Cp}_2\text{Ni}_2(\mu\text{-C}_2\text{Ph}_2)$ (190). Beside the coupled products, μ_3 -alkylidyne $(\mu_3\text{-CPh})\text{Ni}_3\text{Cp}_3$ and $(\mu_3\text{-CR})\text{Co}_3(\text{CO})_9$ were also obtained from the above reactions (189). Catalytic coupling of $\text{Cp}(\text{CO})_2\text{W}(\equiv\text{C}-\text{tolyl})$ in the presence of $\text{Cp}_2\text{Cr}_2(\text{CO})_4$ gives $\text{Cp}(\text{CO})_2\text{W}[\mu\text{-C}_2(\text{tolyl})_2]\text{W}(\text{CO})_2\text{Cp}$ (190). The same bridging acetylene compound is isolated along with $\text{Ni}_2\text{W}(\mu_3\text{-C}-\text{tolyl})(\text{CO})_2\text{Cp}_3$ from the reaction of $\text{Cp}(\text{CO})_2\text{W}(\equiv\text{C}-\text{tolyl})$ with $\text{Ni}_2(\mu\text{-CO})_2\text{Cp}_2$ (191).

Facile Os—Os bond cleavage is observed in the reaction of $\text{Cp}(\text{CO})_2\text{W}(\equiv\text{C}-\text{tolyl})$ with $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ to give a triply bridging acetylene compound in 33% yield [Eq. (114)] (192). The formation of two isomers



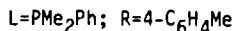
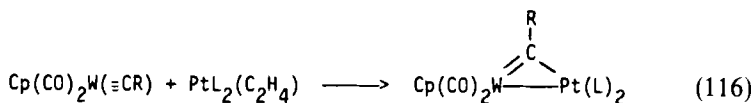
with the bridging acetylene ligand was established by X-ray analysis of the product. The two isomers correspond to two of the three possible potential minima for rotation of the μ_3 -acetylenic moiety on the surface of the triangular W_2Os face. This complex is fluxional at room temperature as evidenced by the singlet at δ 5.06 for the 10 Cp protons (192). Similarly, $Cp(CO)_2W(\equiv C-tolyl)$ reacts with $Os_3(\mu-H)_2(\mu-CH_2)(CO)_{10}$ to give the isomers of the triply bridging acetylene complexes shown in Eq. (114) (4,193,194). The ruthenium analog of the triply bridging acetylene compound is prepared by refluxing $Ru_3(CO)_{12}$ with $Cp(CO)_2W(\equiv CR)$ in toluene [Eq. (114)] (4,193). The carbyne compound $Cp(CO)_2W(\equiv C-R)$ ($R = tolyl$) reacts with $Fe_2(CO)_9$ in ether to give an alkyne-bridged iron-ditungsten cluster $FeW_2(\mu_3-RC_2R)(CO)_6Cp_2$ along with two other products, $Fe_2W(\mu_3-CR)-(\mu-CO)(CO)_8Cp$ and $FeW(\mu-CR)(CO)_6Cp$ [Eq. (115)] (193,195). An X-ray structural study of the alkyne-bridged product shows a semibridging CO and a short W—W distance, 2.747(1) Å, suggesting double bonding. The W—W—C_{alkyne} interaction may be considered a three-center, two-electron bond.



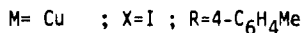
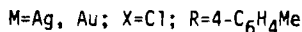
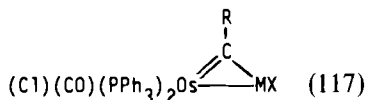
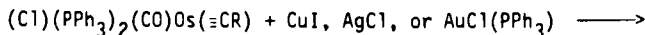
D. Reactions of Carbyne Compounds with Other Metal Complexes

F. G. A. Stone and co-workers (4) have used the isolobal relationship between the $C\equiv C$ bond of organic alkynes and the $M\equiv C$ bond of metal carbyne complexes to prepare a variety of di- and trinuclear complexes. For example, the carbyne compound $Cp(CO)_2W(\equiv C-tolyl)$ shows reactivity toward other transition metal complexes that is similar to that of alkynes (4). This type of carbyne reactivity has been used to prepare a variety of clusters containing doubly and triply bridging carbynes and acetylenes. Coupling of carbynes to give bridging acetylenes was discussed in the previous section [Eqs. (113)–(115)]. F. G. A. Stone has reviewed carbyne reactions which give bridging carbynes up to 1983 (4).

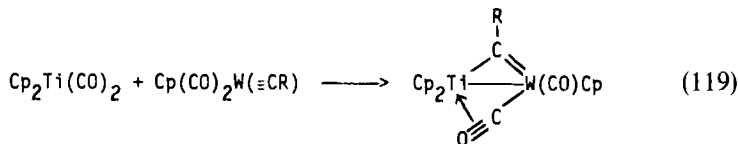
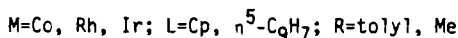
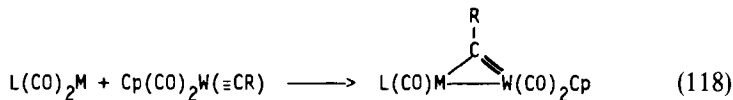
The carbyne compound $Cp(CO)_2W(\equiv C-tolyl)$ reacts with $Pt(C_2H_4)(PMe_2Ph)_2$, displacing ethylene, to give a bridging carbyne compound [Eq. (116)] (196). The related $[HB(pz)_3](CO)_2W(\equiv C-tolyl)$ reacts similarly with $Pt(PMe_3)_2(C_2H_4)$ to give $[HB(pz)_3](CO)_2W(\mu-C-tolyl)Pt(PMe_3)_2$ (55). Addition of CuI , $AgCl$, or $AuCl(PPh_3)$ to the $Os\equiv C$ bond



in $\text{Os}(\equiv\text{C}\text{---tolyl})(\text{CO})(\text{PPh}_3)_2(\text{Cl})$ gives a bridging carbyne compound [Eq. (117)] (197). Because of weak backbonding from the Ag^+ to the carbyne ligand in the AgCl complex, the $\text{Os}(\text{---}\mu\text{---C})$ bond length (1.84 Å) increases by only 0.07 Å on coordination of the AgCl (197). By comparison, greater π -backbonding from the Pt in the product of Eq. (116) increases the $\text{W}(\text{---}\mu\text{---C})$ bond length (1.97 Å) by 0.14 Å (196).



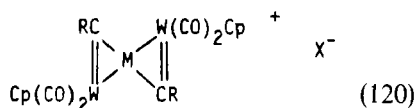
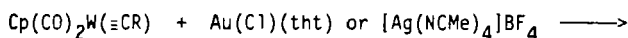
Beside these group 9 and 10 metal compounds, other complexes containing easily displaceable ligands react similarly with the carbyne. Thus, $(\text{C}_6\text{H}_5)_2(\text{CO})_2\text{Cr}(\text{THF})$, $\text{Cp}(\text{CO})_2\text{Re}(\text{THF})$, $(\text{C}_5\text{H}_4\text{Me})(\text{CO})_2\text{Mn}(\text{THF})$, and $\text{Fe}(\text{CO})_4(\text{THF})$ react with $\text{Cp}(\text{CO})_2\text{W}(\equiv\text{C}\text{---tolyl})$ to give doubly bridging carbynes $(\text{C}_6\text{H}_5)_2(\text{CO})_2\text{Cr}(\mu\text{---C}\text{---tolyl})\text{W}(\text{CO})_2\text{Cp}$, $\text{Cp}(\text{CO})_2\text{Re}(\mu\text{---C}\text{---tolyl})\text{W}(\text{CO})_2\text{Cp}$, $(\text{C}_5\text{H}_4\text{Me})(\text{CO})_2\text{Mn}(\mu\text{---C}\text{---tolyl})\text{W}(\text{CO})_2\text{Cp}$, and $(\text{CO})_4\text{Fe}(\mu\text{---C}\text{---tolyl})\text{W}(\text{CO})_2\text{Cp}$, respectively (195,198). Likewise, complexes containing Co, Rh, Ir, Zr, and Ti are obtained by the reactions shown in Eqs. (118) and (119)



(198,199). The analogous carbaborane carbyne $(\eta\text{-}1,2\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)(\text{CO})_2\text{W}(\equiv\text{C}\text{---tolyl})^-$ also reacts with $\text{Rh}(\text{Cl})(\text{PPh}_3)_3$ and $[\text{Rh}(\text{PPh}_3)_2(\text{cod})][\text{BF}_4]$ ($\text{cod} = \text{cycloocta-1,5-diene}$) to give $(\eta\text{-}1,2\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)(\text{CO})\text{W}(\mu\text{-C}\text{---tolyl})\text{---}(\mu\text{-CO})\text{Rh}(\text{PPh}_3)_2$ (157). The formation of a bridging $\mu_2\text{-CR}$ ligand is also observed in the reaction of $\text{Cp}(\text{CO})_2\text{W}(\equiv\text{C}\text{---tolyl})$ with Cp_2V to give $\text{Cp}_2\text{V}(\mu\text{-C}\text{---tolyl})\text{WCp}(\text{CO})_2$ (200).

Because of the isolobal relationship between the $\text{C}\text{---tolyl}$ and $\text{CpW}(\text{CO})_2$ fragments, the alkylidyne complex $\text{Cp}(\text{CO})_2\text{W}(\equiv\text{C}\text{---tolyl})$ may be considered an organometallic analog of an alkyne (4). As such, the products of Eqs. (116)–(119) are analogous to metal–alkyne complexes, and therefore their structures may be viewed as dimetallacycloprenes (4). This is supported by structural data which show relatively short $\text{W}\text{---}(\mu\text{-C})$ bond lengths (about 1.91–1.97 Å), reflecting considerable $\text{W}=\text{C}$ character (196,198–200).

Addition of $\text{Cp}(\text{CO})_2\text{W}(\equiv\text{CR})$ ($\text{R} = \text{tolyl}$) to $\text{Au}(\text{Cl})(\text{tht})$ ($\text{tht} = \text{tetrahydrothiophene}$) in the presence of TiPF_6 affords a gold–tungsten salt $[\text{AuW}_2(\mu\text{-CR})_2(\text{CO})_4\text{Cp}_2][\text{PF}_6]$ [Eq. (120)] (201). The analogous Ag compound is prepared by reaction of $[\text{Ag}(\text{NCMe})_4]\text{BF}_4$ and $\text{Cp}(\text{CO})_2\text{W}(\equiv\text{CR})$

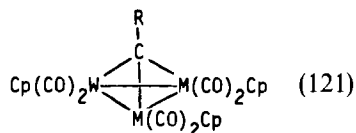
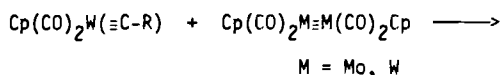


$\text{M} = \text{Au}$; $\text{R} = \text{tolyl}$; $\text{X} = \text{PF}_6$

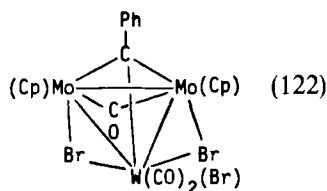
$\text{M} = \text{Ag}$; $\text{R} = \text{tolyl}$; $\text{X} = \text{BF}_4$

[Eq. (120)] (201). An X-ray structural analysis of the Au compound shows that the cation has a bent $\text{W}\text{---Au}\text{---W}$ spine [$162.8(1)^\circ$] with the $\text{Au}\text{---W}$ bonds bridged by the $\text{C}\text{---tolyl}$ groups (201). The dihedral angle between the two dimetallacycloprenes rings is 62° . The analogous neutral Pt compound ($\text{M} = \text{Pt}$) is prepared from the reaction of $\text{Cp}(\text{CO})_2\text{W}(\equiv\text{CR})$ and $\text{Pt}(\text{C}_2\text{H}_4)_3$ in a 2:1 molar ratio (202).

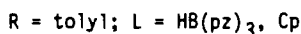
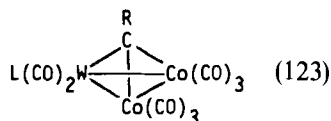
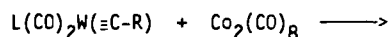
It is well known that $\text{M}_2(\text{CO})_4\text{Cp}_2$ complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), which formally contain $\text{M}\equiv\text{M}$ bonds, readily add alkynes to give bridging alkyne compounds $\text{M}_2(\mu\text{-RC}_2\text{R})(\text{CO})_4\text{Cp}_2$ (203). Similarly, $\text{M}_2(\text{CO})_4\text{Cp}_2$ ($\text{M} = \text{Mo}, \text{W}$) react with $\text{Cp}(\text{CO})_2\text{W}(\equiv\text{C}\text{---R})$ in toluene at 100°C to give triply bridging carbyne compounds according to Eq. (121) (190). In contrast, $\text{Cp}_2(\text{CO})_4\text{Cr}_2$ and the carbyne $\text{Cp}(\text{CO})_2\text{W}(\equiv\text{CR})$ ($\text{R} = \text{tolyl}$) afford the μ -alkyne–ditungsten compound $\text{Cp}(\text{CO})_2\text{W}(\mu\text{-RC}_2\text{R})\text{W}(\text{CO})_2\text{Cp}$; this reaction is catalyzed by small amounts of the dichromium species (190). The



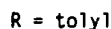
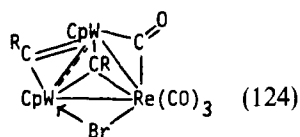
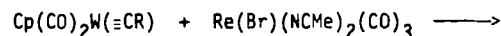
$\text{W}\equiv\text{C}$ bond in $(\text{Br})(\text{CO})_4\text{W}(\equiv\text{C}-\text{Ph})$ also adds to $\text{M}\equiv\text{M}$ in $\text{Cp}(\text{CO})_2\text{Mo}\equiv\text{Mo}(\text{CO})_2\text{Cp}$ to give a μ_3 -carbyne trinuclear metal cluster in 20% yield [Eq. (122)] (204). Some complications are involved in this reaction



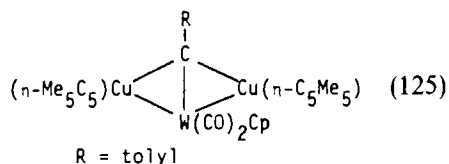
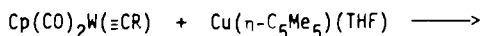
since the Br/W ratio in the product (3:1) is greater than that in the reactant (1:1). The analogous cobalt μ_3 -carbyne trinuclear cluster is prepared by reaction of $\text{Co}_2(\text{CO})_8$ with $\text{L}(\text{CO})_2\text{W}(\equiv\text{C}-\text{tolyl})$ ($\text{L} = \text{HB}(\text{pz})_3$, Cp) [Eq. (123)] (55,205). Similarly, the reaction of $\text{Cp}(\text{CO})_2\text{W}(\equiv\text{C}-\text{tolyl})$ with



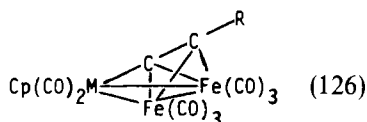
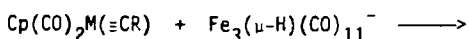
$\text{Re}_2(\text{CO})_{10}$ produces the μ_3 -bridging carbyne trinuclear WRe_2 cluster $\text{Cp}(\text{CO})_2\text{W}(\mu_3\text{-C}-\text{tolyl})\text{Re}_2(\text{CO})_8$ (206). The $\text{Cp}(\text{CO})_2\text{W}(\equiv\text{C}-\text{R})$ carbyne reacts with $\text{Re}(\text{Br})(\text{NCMe})_2(\text{CO})_3$ to yield a trinuclear cluster with μ_2 - and μ_3 -carbyne ligands [Eq. (124)] (206). An X-ray structure of the product shows a ReW_2 triangle which is capped by a C—tolyl ligand and is edge-



bridged by C—tolyl, Br, and CO groups (206). Reaction of the carbyne compound with $\text{Cu}(\eta\text{-C}_5\text{Me}_5)(\text{THF})$ gives a μ_3 -carbyne compound according to Eq. (125) (207).



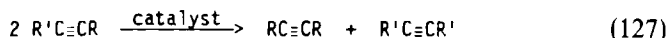
In contrast to its previously discussed reactions, the $\text{M}\equiv\text{C}$ bond of $\text{Cp}(\text{CO})_2\text{M}(\equiv\text{CR})$ ($\text{R} = \text{Me, tolyl}$; $\text{M} = \text{Mo, W}$) is cleaved on reaction with $[\text{Et}_3\text{NH}][\text{Fe}_3(\mu\text{-H})(\text{CO})_{11}]$ (208) to give acetylide-bridged complexes $\text{Fe}_2\text{M}(\mu\text{-C}_2\text{R})(\text{CO})_8\text{Cp}$ in about 30% yield [Eq. (126)] (208). Studies of the carbyne



compound with ^{13}C -labeled carbyne and CO ligands showed that $\text{M}\equiv\text{C}$ bonds are broken in this reaction and the $\mu_3\text{-C}$ atom is derived from a CO ligand. Scrambling of CO groups between tungsten and iron is also observed.

E. Alkyne Metathesis and Reactions with Acetylenes

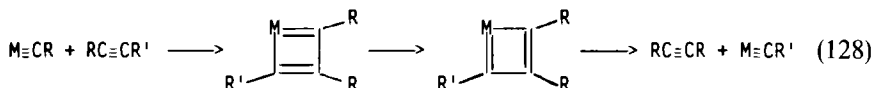
Alkynes can be metathesized by heterogeneous [e.g., $\text{WCl}_6\text{-AlEtCl}_2$, $\text{WCl}_6\text{-Al}(i\text{-C}_4\text{H}_9)_3$] (209,210) and homogeneous [e.g., $\text{Mo}(\text{CO})_6/\text{phenol}$, $\text{MoO}_2(\text{acac})_2\text{-AlEt}_3\text{-PhOH}$] (211) catalysts [Eq. (127)]. A mechanism involving transition metal alkylidyne and metallacyclobutadiene intermediates



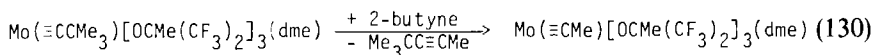
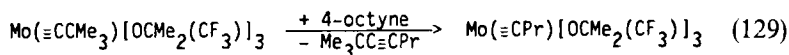
was proposed for this reaction by Katz and McGinnis (8). EPR studies of heterogeneous alkyne metathesis catalysts also support the existence of alkylidyne intermediates (9). Schrock and co-workers (212,213) found that tungsten(VI) alkylidyne complexes catalyze the metathesis of disubstituted alkynes at rates far greater than those reported for the aforementioned homogeneous and heterogeneous catalysts.

1. Alkyne Metathesis

Fischer-type carbynes such as $(\text{Br})(\text{CO})_4\text{W}(\equiv\text{CPh})$ are not alkyne metathesis catalysts, whereas Schrock and co-workers have shown that $(\text{Me}_3\text{CO})_3\text{W}(\equiv\text{C}-\text{CMe}_3)$ does catalytically metathesize $\text{EtC}\equiv\text{CPh}$ and $\text{PrC}\equiv\text{CPh}$ via unstable tungstenacyclobutadiene intermediates [Eq. (128)]



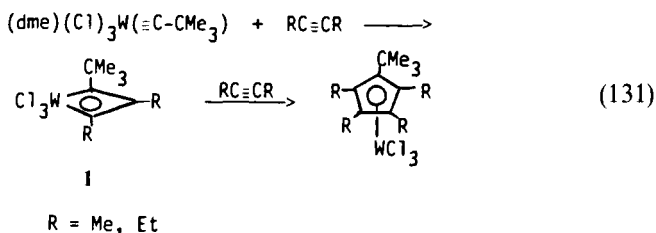
(212–214). The analogous molybdenum complex, however, does not react with acetylenes (215). It appears that Mo in $\text{Mo}(\equiv\text{CCMe}_3)(\text{OCMe}_3)_3$ is not electrophilic enough compared to W in $\text{W}(\equiv\text{CCMe}_3)(\text{OCMe}_3)_3$. However, Mo carbyne compounds with more electron-withdrawing alkoxide ligands, $\text{Mo}(\equiv\text{C}-\text{CMe}_3)[\text{OCMe}_2(\text{CF}_3)]_3$ and $\text{Mo}(\equiv\text{CCMe}_3)[\text{OCMe}(\text{CF}_3)_2]_3(\text{dme})$ ($\text{dme} = 1,2\text{-dimethoxyethane}$), do undergo metathesis with acetylenes [Eqs. (129) and (130)] (215,216). Analogous carbyne compounds



$\text{Mo}(\equiv\text{CCMe}_3)(\text{O}-i\text{-Pr})_3$ and $\text{Mo}(\equiv\text{CCMe}_3)(\text{OCH}_2\text{CMe}_3)_3$ with relatively small alkoxide ligands polymerize acetylenes; it has been suggested that the small alkoxide ligands allow more acetylenes to react with the molybdenacyclobutadiene intermediate to give polymers (215,216). Clearly the auxiliary ligands in carbyne compounds play an important role in determining catalytic activity in alkyne metathesis reactions.

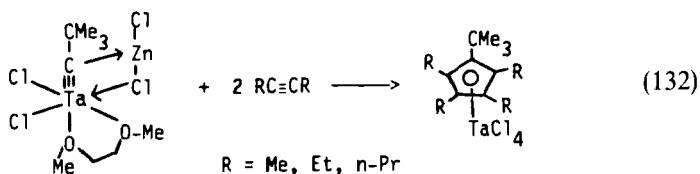
2. Reactions with Acetylenes

As noted in the previous section, $(\text{Me}_3\text{CO})_3\text{W}(\equiv\text{C}-\text{CMe}_3)$ catalytically metathesizes dialkylacetylenes (212–214). On the other hand, $\text{W}(\equiv\text{C}-\text{CMe}_3)(\text{CH}_2\text{CMe}_3)_3$, $\text{W}(\equiv\text{C}-\text{CMe}_3)(\text{dme})(\text{Cl})_3$ ($\text{dme} = 1,2\text{-dimethoxyethane}$), and $[\text{NEt}_4][\text{W}(\equiv\text{C}-\text{CMe}_3)\text{Cl}_4]$ do not (217); however, they do react with acetylenes. For example, $(\text{dme})(\text{Cl})_3\text{W}(\equiv\text{C}-\text{CMe}_3)$ reacts with 3-hexyne and 2-butyne to yield planar, delocalized tungstenacyclobutadiene complexes, which are stable toward reformation of the alkylidyne complex, but with a second equivalent of 3-hexyne and 2-butyne give cyclopentadienyl complexes [Eq. (131)] (217,218). These cyclopentadienyl complexes can combine with another acetylene to give $\text{W}(\eta^5\text{-C}_5\text{R}_4\text{CMe}_3)(\text{RC}\equiv\text{CR})(\text{Cl})_2$ (217).



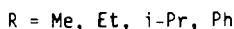
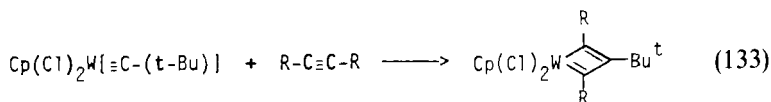
Interestingly, the alkyne metathesis activity of $(\text{Me}_3\text{CO})_3\text{W}(\equiv\text{CCMe}_3)$ discussed in the previous section eventually ceases (in days), and when it does, catalytically inactive cyclopentadienyl complexes can be isolated (217). These observations support the involvement of metallacyclobutadienes as possible intermediates in alkyne metathesis reactions.

A ZnCl_2 adduct of a tantalum alkylidyne complex $[\text{Cl}_2(\text{MeOCH}_2\text{CH}_2\text{OMe})\text{Ta}(\mu\text{-CCMe}_3)]_2\text{Zn}(\mu\text{-Cl})_2$ also reacts with acetylenes to give a cyclopentadienyl complex [Eq. (132)] (219). A number of metallacyclobutadiene compounds, analogs of **1** containing different ring substituents



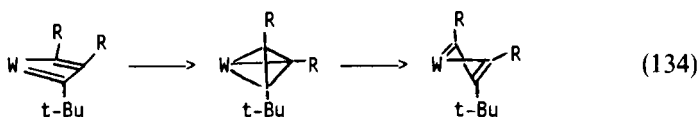
and/or containing alkoxy ligands, have been synthesized via reactions of carbyne complexes with acetylenes, structurally characterized, and shown to metathesize alkynes; for example, $(\text{RO})_3\text{W}(\text{C}_3\text{R}'_3)$ [$\text{R} = \text{CMe}(\text{CF}_3)_2$, $\text{R}' = \text{Me}$ or Et] catalyze the metathesis of 3-heptyne (220–222).

Reactions between $\text{CpW}(\equiv\text{CCMe}_3)(\text{Cl})_2$ and disubstituted acetylenes yield tungstenacyclobutadiene compounds [Eq. (133)]; an X-ray structure of

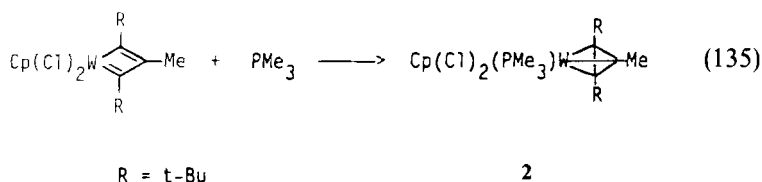


the diphenylacetylene product shows that the metallacyclobutadiene ring contains localized double and single bonds and is puckered; the phenyl groups are on the α -carbons. The WC_3 ring conformation is intermediate between being planar and having a metallatetrahedrane η^3 -cyclopropenyl structure. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at room temperature exhibits a single broad resonance for all three WC_3 ring carbon atoms. It is proposed that this is caused by scrambling on the metal via a fluxional process involving formation

of a tungsten cyclopropenyl intermediate [Eq. (134)] (223). Supporting the above mechanism is the conversion of the metallacyclobutadiene complex

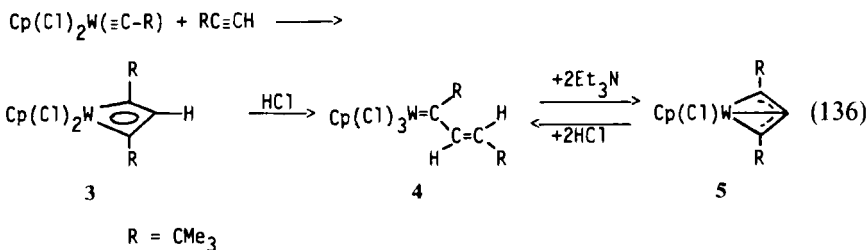


$\text{Cp}(\text{Cl})_2\text{W}[\text{C}_2(\text{CMe}_3)_2\text{CMe}]$ to an η^3 -cyclopropenyl compound on treatment with PMe_3 [Eq. (135)] (224). NMR studies of **2** showed that the C_3 ring does

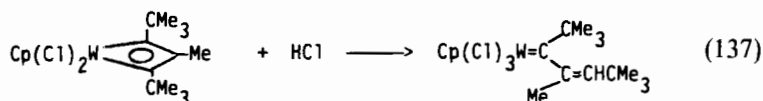


not rotate rapidly about the W-ring axis on the NMR time scale at room temperature (224). Similarly, addition of nitrogen donor ligands to the planar metallacyclobutadiene compound, $\text{Cl}_3\text{W}[\text{C}_3\text{Me}_2(\text{t-Bu})]$ (**1**), results in ring closure to yield the η^3 -cyclopropenyl compounds $\text{Cl}_3\text{W}[\eta^3\text{-C}_3\text{Me}_2(\text{t-Bu})]\text{L}_2$ ($\text{L} = \text{pyridine}$, $\text{L}_2 = \text{tetramethylethylenediamine}$) (225).

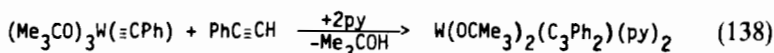
$\text{CpW}(\equiv\text{C}-\text{CMe}_3)(\text{Cl})_2$ reacts with the terminal alkyne $\text{Me}_3\text{CC}\equiv\text{CH}$ to give approximately equal amounts of two products, $\text{CpW}[\text{C}_3\text{H}_2(\text{CMe}_3)_2]\text{Cl}_3$ (**4**) and $\text{CpW}[\text{C}_3(\text{CMe}_3)_2]\text{Cl}$ (**5**), in high yield [Eq. (136)]



(226). Compound **5** can be converted to **4** on treatment with HCl. If triethylamine is present in the reaction between $\text{CpW}(\equiv\text{C}-\text{CMe}_3)(\text{Cl})_2$ and $\text{Me}_3\text{CC}\equiv\text{CH}$, only **5** is produced along with NEt_3HCl . The proposed intermediate **3** is reasonable based on the fact that $\text{Cp}(\text{Cl})_2\text{W}[\text{C}_3(\text{CMe}_3)_2\text{Me}]$ reacts with 1 equivalent of HCl to give a complex analogous to **4** [Eq. (137)] (226). A complex similar to **3** is prepared in the reaction of $\text{W}(\equiv\text{C}-\text{CMe}_3)[\text{OCH}(\text{CF}_3)_2]_3$ and $\text{Me}_3\text{CC}\equiv\text{CH}$; an X-ray structural analysis of the product $\text{W}[\text{C}(\text{t-Bu})\text{CHC}(\text{t-Bu})][\text{OCH}(\text{CF}_3)_2]_3$ shows that the tungstenacyclobutadiene ring is planar and delocalized (227). An X-ray

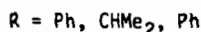
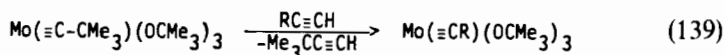


structural study of **5** shows that it is a dehydrohalogenated version of its likely tungstenacyclobutadiene precursor **3** (226). A compound analogous to **5** is formed from the reaction of $(\text{Me}_3\text{CO})_3\text{W}(\equiv\text{CPh})$, an active alkyne metathesis complex, and $\text{PhC}\equiv\text{CH}$ [Eq. (138)] (226). Recently, it was reported that $\text{Mo}(\equiv\text{CCMe}_3)(\text{O}_2\text{CCF}_3)_3(\text{dme})$ also reacts with $\text{RC}\equiv\text{CH}$

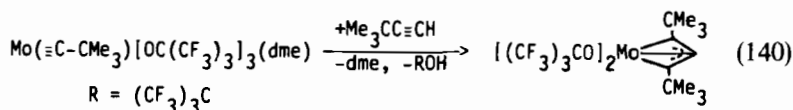


($\text{R} = \text{CMe}_3, \text{Ph}$) to give the deprotonated molybdenacyclobutadiene complexes $\text{Mo}[\text{C}_3(\text{CMe}_3)(\text{R})](\text{O}_2\text{CCF}_3)_2(\text{dme})$ with elimination of $\text{CF}_3\text{CO}_2\text{H}$ (228). Thus, a proton can be readily lost from a carbon atom in the tungstenacyclobutadiene moiety; this might be the reason why terminal alkynes have not been metathesized successfully.

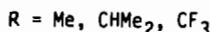
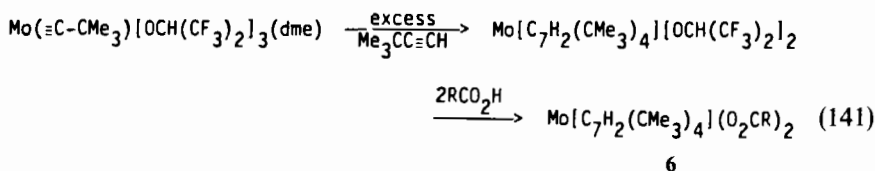
Reactions between $\text{Mo}(\equiv\text{CCMe}_3)(\text{OCMe}_3)_3$ and terminal acetylenes $\text{RC}\equiv\text{CH}$ yield metathesized products [Eq. (139)] (216), whereas the fluoroalkoxy neopentylidyne compounds react with $\text{Me}_3\text{CC}\equiv\text{CH}$ to give a

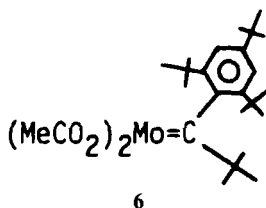


deprotonated molybdenacyclobutadiene compound [Eq. (140)] (216). In the presence of excess $\text{Me}_3\text{CC}\equiv\text{CH}$, the analogous compound $\text{Mo}(\equiv\text{CCMe}_3)[\text{OCH}(\text{CF}_3)_2]_3(\text{dme})$ reacts to give $\text{Mo}[\text{C}_7\text{H}_2(\text{CMe}_3)_4][\text{OCH}(\text{CF}_3)_2]_2$, which subsequently undergoes ligand substitution to yield



$\text{Mo}[\text{C}_7\text{H}_2(\text{CMe}_3)_4](\text{O}_2\text{CR})_2$ [Eq. (141)] (229). An X-ray structural study of **6** shows that it is best described as containing an alkylidyne group

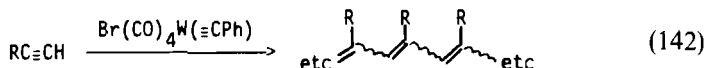




with *tert*-butyl and η^4 -2,4,6-tri-*tert*-butylphenyl groups attached to the alkylidene carbon atom (229). It is proposed to form via sequential insertion of two $\text{Me}_3\text{CC}\equiv\text{CH}$ units into the $\text{Mo}-\text{C}_\alpha$ bond of a deprotonated molybdenacyclobutadiene compound.

F. Polymerization of Acetylenes and Cyclic Olefins

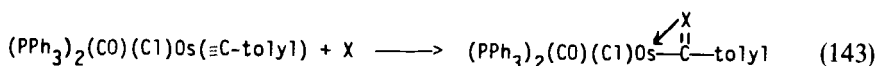
As mentioned earlier, $(\text{Br})(\text{CO})_4\text{W}(\equiv\text{C}-\text{Ph})$ does not catalyze alkyne metathesis. But $(\text{Br})(\text{CO})_4\text{W}(\equiv\text{C}-\text{Ph})$, $(\text{Br})(\text{CO})_4\text{W}(\equiv\text{CMe})$, and $\text{Cp}(\text{CO})_2\text{-W}(\equiv\text{C}-\text{Ph})$ do catalyze the polymerization of acetylenes and cycloalkenes [Eq. (142)]; $\text{HC}\equiv\text{CH}$, monosubstituted and disubstituted acetylenes, as



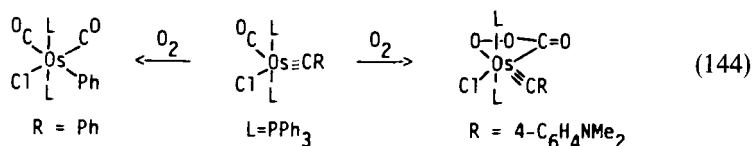
well as acetylenes with functional groups (CN, ester, halogen) remote from the triple bond have all been polymerized (230). The polymetathesis of cycloalkenes (cyclopentene, cycloheptene, cyclooctene, norbornene) is accelerated by O_2 , yielding polyalkenamers whose double bonds are largely *cis* (230). The carbene compound $(\text{CO})_5\text{W}[\equiv\text{C}(\text{OMe})(\text{Ph})]$ can also be used as an initiator for the polymerization of acetylenes and norbornene, which suggests that the metal carbyne is simply a source for the metal carbene catalyst (230). The molybdenum carbynes $\text{Mo}(\equiv\text{CCMe}_3)(\text{O}-i\text{-Pr})_3$ and $\text{Mo}(\equiv\text{CCMe}_3)(\text{OCH}_2\text{CMe}_3)_3$ polymerize 3-heptyne (215,216). The combination of $(\text{X})(\text{CO})_4\text{W}(\equiv\text{CR})$ ($\text{X} = \text{Cl}, \text{Br}; \text{R} = \text{Me}, \text{Ph}$) and MCl_4 ($\text{M} = \text{Ti}, \text{V}, \text{W}, \text{Sn}$) also polymetathesizes cycloalkenes (231). Also, $(\text{Br})(\text{CO})_4\text{W}(\equiv\text{CPh})/\text{Et}_2\text{AlCl}$ efficiently polymerizes norbornenes (232).

G. Reactions with Chalcogenides

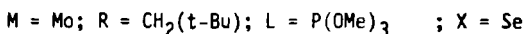
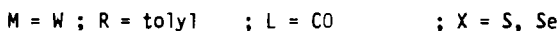
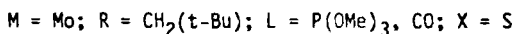
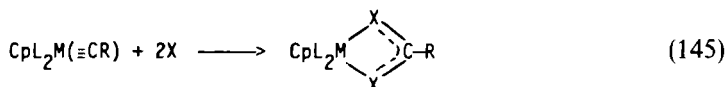
Reactions of the osmium carbyne compound in Eq. (143) with S, Se, and Te give η^2 -thio-, seleno-, and telluroacyl complexes $\text{Os}[\eta^2\text{-C}(=\text{X})\text{R}](\text{Cl})(\text{CO})(\text{PPh}_3)_2$ [Eq. (143)] (67). However, when the phenylcarbyne complex



$(\text{PPh}_3)_2(\text{CO})(\text{Cl})\text{Os}(\equiv\text{CPh})$ is exposed to O_2 at 0°C , only $\text{Os}(\text{Cl})(\text{Ph})(\text{CO})_2-(\text{PPh}_3)_2$ is isolated in high yield [Eq. (144)] (68). In contrast, the *p*-dimethylaminophenylcarbyne complex $(\text{PPh}_3)_2(\text{CO})(\text{Cl})\text{Os}(\equiv\text{C}-\text{C}_6\text{H}_4\text{NMe}_2-4)$ reacts with O_2 to give the η^2 -peroxycarbonyl compound [Eq. (144)] (68). In



reactions of $\text{CpL}_2\text{M}(\equiv\text{CR})$ with S and Se [Eq. (145)] (233), the carbyne (CR) is converted to $\eta^2\text{-X}_2\text{CR}$ ($\text{X} = \text{S}, \text{Se}$); the presence of the $\eta^2\text{-X}_2\text{CR}$ ligand was established by X-ray crystallography.



H. Substitution of the Carbyne R Group in $\text{L}_n\text{M}\equiv\text{C}-\text{R}$

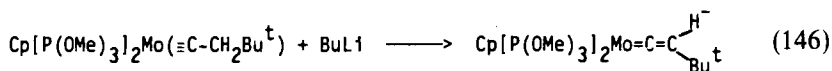
As mentioned earlier in Section IV,A, nucleophiles can add to carbyne carbon atoms to give carbene complexes [Eq. (60)]. However, in the case of the only known chlorocarbyne compound, nucleophilic displacement of Cl^- is observed due to the good leaving group ability of Cl^- [Eq. (33)]; this reaction provides a good synthetic route to thio- and selenocarbynes (43).

I. Transformation of Carbynes into Vinylidenes

1. Deprotonation of a β -Hydrogen

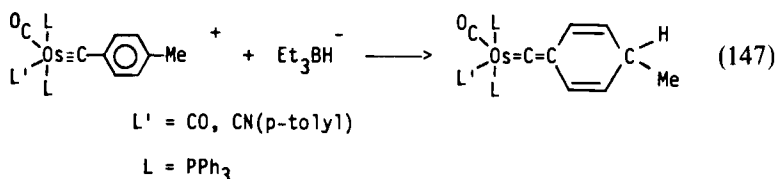
Deprotonation of $\text{Cp}[\text{P}(\text{OMe})_3]_2\text{Mo}(\equiv\text{C}-\text{CH}_2\text{Bu}')$ with *n*-BuLi leads to the formation of an anionic vinylidene compound [Eq. (146)]

(234). Similarly, deprotonation of the cationic carbyne *mer*-(dppe)(CO)₃W-(≡C—CHMePh)⁺ gives the corresponding neutral vinylidene complex (110).



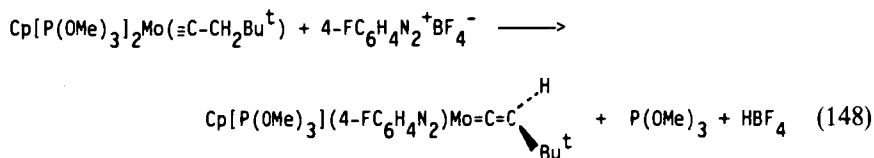
2. Hydride Addition

A cationic phenyl carbyne compound is converted to an unusual vinylidene by reaction with Li(Et₃BH) [Eq. (147)] (235).

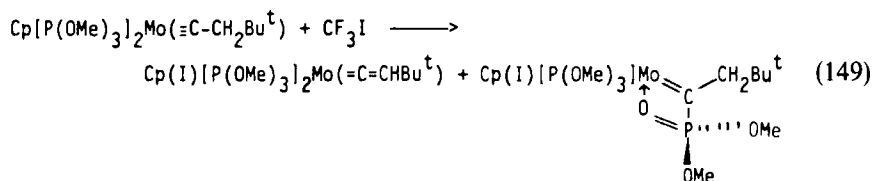


3. Oxidative Conversion

The reaction of Cp[P(OMe)₃]₂Mo(≡C—CH₂Bu^t) with the aryldiazonium salt 4-FC₆H₄N₂⁺BF₄⁻ yields a vinylidene compound according to Eq. (148) (236). An oxidative reaction of Cp[P(OMe)₃]₂Mo(≡C—CH₂Bu^t)

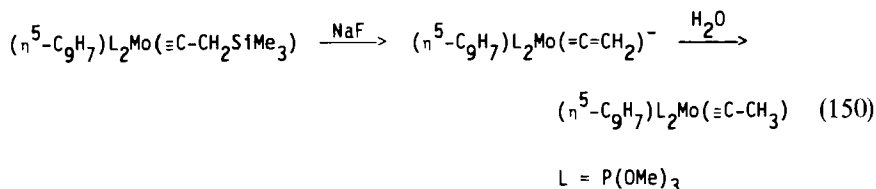


with CF₃I gives a vinylidene compound [Eq. (149)] (236). This reaction has been proposed to proceed by initial oxidative addition of CF₃I to the Mo followed by elimination of a proton as HCF₃. The second product in Eq. (149) is presumably formed by an Arbuzov reaction followed by migration of the phosphonate group from the molybdenum to the alkylidyne carbon.



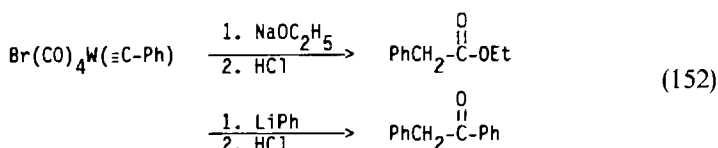
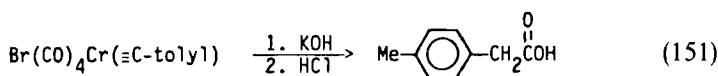
4. Carbon-Silicon Heterolysis

Removal of the SiMe_3 group with NaF from $(\eta^5\text{-C}_9\text{H}_7)[\text{P}(\text{OMe})_3]_2\text{Mo}(\equiv\text{C}-\text{CH}_2\text{SiMe}_3)$ generates an anionic vinylidene, which then reacts rapidly with water to afford a carbyne compound [Eq. (150)] (111).

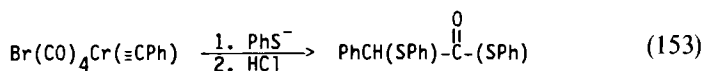


J. Cleavage of Carbyne Ligands from Metals

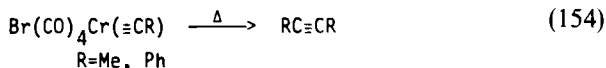
Carbyne ligands are cleaved from metals as organic carboxylic acids, esters, and ketones according to Eqs. (151) and (152) (237). The first step in these reactions probably involves attack of the nucleophile at the C atom of a CO to

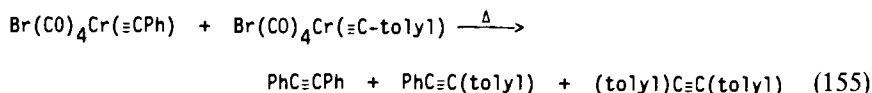


give an acyl intermediate, $(\text{L})\text{M}(\equiv\text{C-R})[\text{C}(=\text{O})\text{Nu}]$. The next step could involve transfer of the resulting acylate group onto the carbyne carbon atom, followed by reductive elimination of the organic product on protonation by acid. A somewhat different type of product results from the reaction of SPh^- and HCl with $(\text{Br})(\text{CO})_4\text{Cr}(\equiv\text{C-Ph})$ [Eq. (153)] (238). Initial double attack

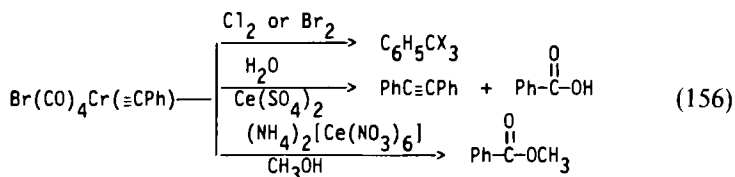


by PhS^- on both CO carbon and the carbyne carbon could lead to the product. Coupling of two carbyne moieties to form acetylenes occurs during the thermolysis of certain carbyne compounds [Eqs. (154) and (155)] (239).



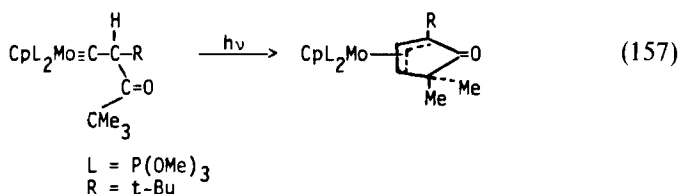


Oxidizing agents cleave the carbyne ligand from $\text{Br}(\text{CO})_4\text{Cr}(\equiv\text{CPh})$ to yield various organic products [Eq. (156)] (240).

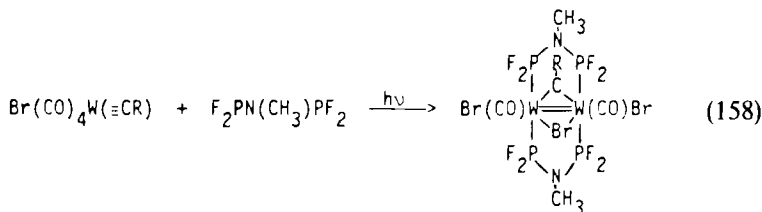


K. Photochemical Reactions

In contrast to extensive studies of the photochemical reactions of alkyl and alkylidene complexes (241), only a few alkylidyne complexes, *trans*- $\text{Cl}(\text{CO})_4\text{W}(\equiv\text{C-tolyl})$ (242), $(\text{CO})_2(\text{PPh}_3)_2\text{Os}(\equiv\text{CPh})^+$ (243), and $(\text{CO})-(\text{PPh}_3)_2(\text{Cl})\text{Os}(\equiv\text{CPh})$ (243), have been examined under photolysis. These reactions were recently included in a review by Pourreau and Geoffroy (241). A more recent example is that involving the photolysis of $\text{Cp}[\text{P}(\text{OMe})_3]_2\text{Mo}\{\equiv\text{C-CH}(t\text{-Bu})[\text{C}(=\text{O})(t\text{-Bu})]\}$ to give a five-membered ring product by intramolecular carbon-hydrogen activation [Eq. (157)] (106). The

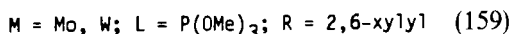
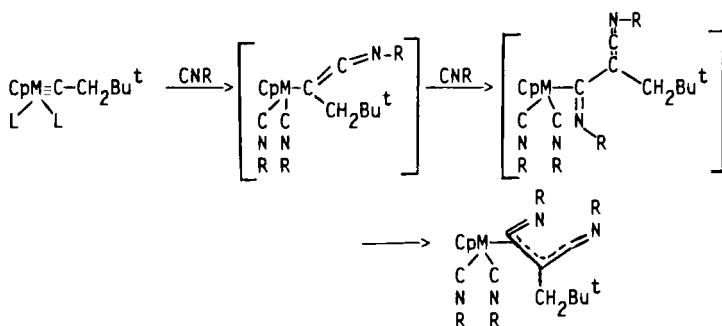


product was characterized by X-ray crystallography. Photolysis of $\text{Br}(\text{CO})_4\text{W}(\equiv\text{C-tolyl})$ with $\text{F}_2\text{PN}(\text{CH}_3)\text{PF}_2$ gives, in 14% yield, the unusual bridging carbyne complex shown in Eq. (158) (244). The crystal structure of this complex shows it to contain a W-W double bond 2.623(5) Å, which is confirmed by the diamagnetism of the compound.



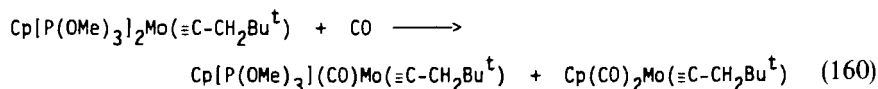
L. Miscellaneous Reactions

In a remarkable reaction, $\text{Cp}[\text{P}(\text{OMe})_3]_2\text{M}(\equiv\text{C}-\text{CH}_2\text{Bu}^t)$ ($\text{M} = \text{Mo}, \text{W}$) combines with four molecules of xylisocyanide [Eq. (159)] (245). Two of the isocyanide ligands replace the two phosphite ligands, and two isocyanides are incorporated into the carbyne portion of the complex [Eq. (159)] (245). A possible mechanism [Eq. (159)] involves a keteneiminyll intermediate, resulting from the addition of an isocyanide to the carbyne carbon. The

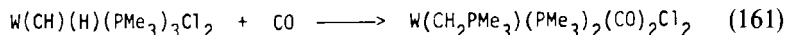


keteneiminyll intermediate could undergo CNR insertion, followed by rearrangement to the final product.

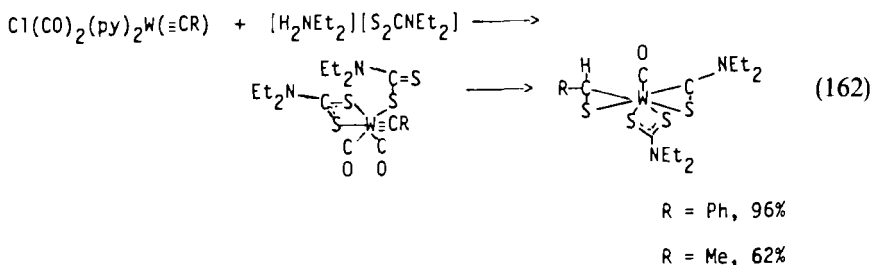
In contrast to the reaction with xylisocyanide, CO simply replaces the phosphite ligands to give CO-substituted products [Eq. (160)] (245). The



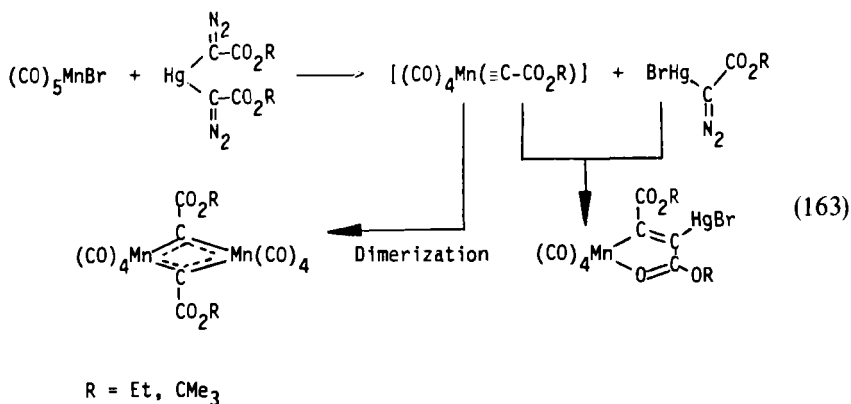
reaction of $\text{W}(\equiv\text{CH})(\text{H})(\text{PMe}_3)_3(\text{Cl})_2$ with CO (30 psi) gives a methylenephosphorane complex [Eq. (161)] (60); the CO apparently promotes migration of the H and PMe_3 ligands onto the carbyne carbon atom.



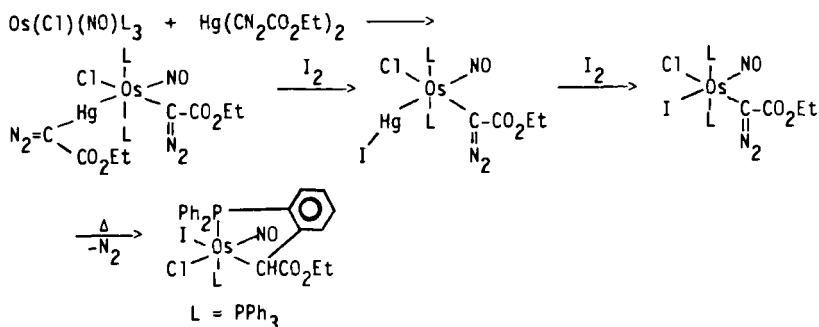
Mayr and co-workers found that $\text{Cl}(\text{CO})_2(\text{py})_2\text{W}(\equiv\text{CR})$ reacts with $[\text{H}_2\text{NET}_2][\text{S}_2\text{CNET}_2]$ to give in high yield a complex with the rare thioaldehyde ligand [Eq. (162)] (167). The mechanism of this reaction presumably involves protonation of the anionic carbyne intermediate by the H_2NET_2^+ to give $(\text{Et}_2\text{NCS}_2)(\text{CO})_2\text{W}(=\text{CHR})$. Loss of CO followed by transfer of a sulfur atom from one of the dithiocarbamate (Et_2NCS_2) ligands to the carbene carbon would result in the formation of the final product.



Reaction of $(\text{CO})_5\text{MnBr}$ with mercuridiazalkanes $\text{Hg}(\text{CN}_2\text{CO}_2\text{R})_2$ gives two products [Eq. (163)] (246). A carbyne complex is proposed as an intermediate [Eq. (163)]; its dimerization would lead to the dinuclear bridging carbyne product, whereas carbyne-carbene coupling would result in the formation of the second product.



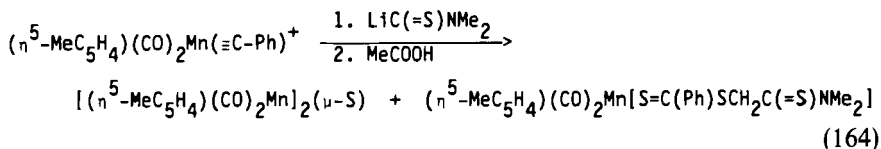
Roper and co-workers reported the reaction of $\text{Os}(\text{Cl})(\text{NO})(\text{PPh}_3)_3$ and $\text{Hg}(\text{CN}_2\text{CO}_2\text{Et})_2$ to give the simple oxidative addition product according to Scheme 3 (247). This product undergoes cleavage of the Os—Hg bond on



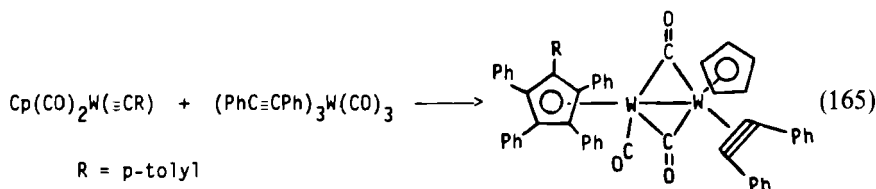
SCHEME 3

reaction with I_2 according to Scheme 3. On warming, the diazoalkylosmium complex loses N_2 and yields the metallacyclic product. It is proposed that an intermediate carbyne complex, resulting from loss of N_2 , $[(Cl)(NO)(PPh_3)_2-Os(\equiv C-CO_2Et)]I$ undergoes intramolecular insertion into an ortho C—H bond of the PPh_3 (Scheme 3).

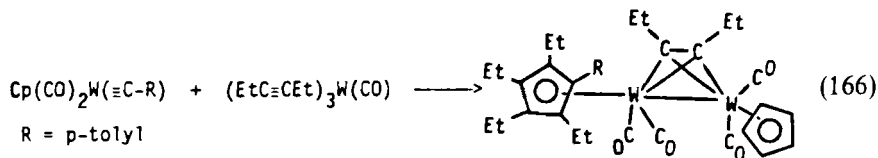
The reaction of $(\eta^5-MeC_5H_4)(CO)_2Mn(\equiv C-Ph)^+$ with $LiC(=S)NMe_2$ gives two products in very low yield (6%, 4%) [Eq. (164)] (248). The mechanism of this reaction is not clear.



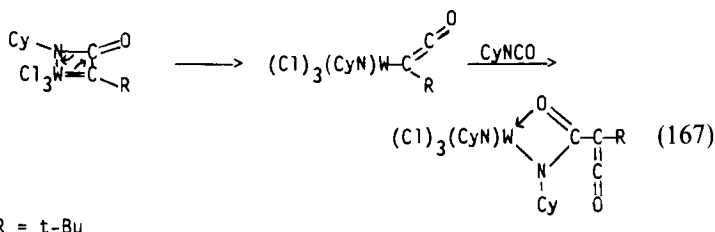
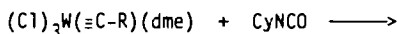
The carbyne compound $Cp(CO)_2W(\equiv C-R)$ ($R = p$ -tolyl), reacts with $(PhC\equiv CPh)_3W(CO)$ to give a ditungsten compound in 26% yield according to Eq. (165) (249). The $\eta^5-C_5Ph_4R$ ring is proposed to form from two acetylene ligands and the carbyne fragment. The diethyacetylene compound



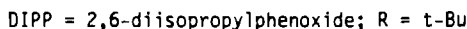
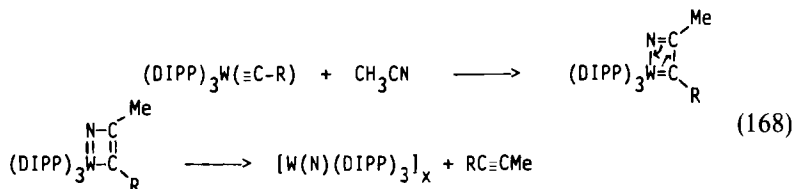
$(EtC\equiv CEt)_3W(CO)$ reacts with the same carbyne $Cp(CO)_2W(\equiv C-R)$ to give a bridging acetylene complex [Eq. (166)] (249). The differences in the product structures in Eqs. (165) and (166) might be due to the greater steric bulk of the phenyl rings.



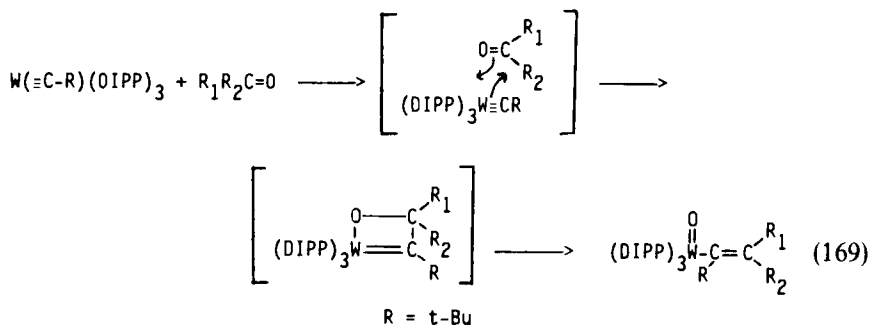
Addition of 2 equivalents of cyclohexyl isocyanate to $(Cl)_3W(\equiv C-t-Bu)-(dme)$ yields $(Cl)_3(NCy)W[N(Cy)C(O)C(CO)(t-Bu)]$ according to Eq. (167) (250). The structure of the product was determined by an X-ray diffraction investigation. It is proposed that the first step in the reaction involves formation of an intermediate containing a cyclohexylimido and a ketenyl ligand [Eq. (167)]. A second cyclohexyl isocyanate then inserts into the tungsten-carbon single bond of the ketenyl ligand to form the final product [Eq. (167)]



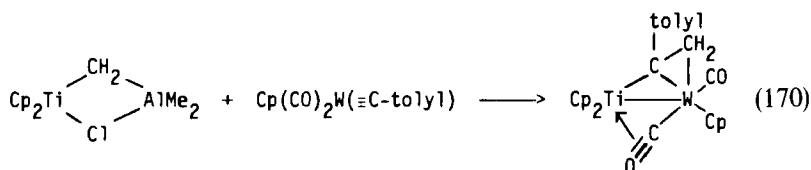
A similar Wittig-like reaction is observed when $\text{W}(\equiv\text{C}-t\text{-Bu})(\text{DIPP})_3$ ($\text{DIPP} = 2,6\text{-diisopropylphenoxide}$) reacts with CH_3CN to give $[\text{W}(\text{N})(\text{DIPP})_3]_x$ and $t\text{-BuC}\equiv\text{CMe}$ [Eq. (168)] (251). By analogy with tungstenacyclobutadiene intermediates in acetylene methathesis [Eq. (128)], the



intermediate in this reaction is proposed to be an azatungstenacyclobutadiene complex [Eq. (168)]. The carbyne compound $\text{W}(\equiv\text{C}-t\text{-Bu})(\text{DIPP})_3$ reacts with Me_2CO , CH_2O , PhCHO , EtOCHO , and Me_2NCHO to give oxo vinyl complexes of the type $\text{W}(\text{O})(t\text{-BuC}=\text{CR}_1\text{R}_2)(\text{DIPP})_3$ [Eq. (169)] (251). The reaction probably involves nucleophilic attack at the carbonyl carbon atom by the alkylidyne carbon to give an oxytungstenacyclobutene intermediate which then rearranges to the final product [Eq. (169)].



Methylene group transfer from titanium to tungsten is observed in the reaction of $\text{Cp}_2\text{Ti}(\text{Cl}\cdot\text{AlMe}_2\cdot\text{CH}_2)$ with $\text{Cp}(\text{CO})_2\text{W}(\equiv\text{C}-\text{tolyl})$ [Eq. (170)]



(252). The product is formed in 50% yield; half an equivalent of the tolyldiyne tungsten species remains unreacted. Based on the apparent stoichiometry in this reaction, it is proposed that reaction of the carbyne compound with the first equivalent of $\text{Cp}_2\text{Ti}(\text{Cl} \cdot \text{AlMe}_2 \cdot \text{CH}_2)$ gives $\text{Cp}_2\text{Ti}(\mu\text{-C-tolyl})\text{W}(\text{CO})_2\text{Cp}$, while the second equivalent transfers a methylene group to $\text{Cp}_2\text{Ti}(\mu\text{-C-tolyl})\text{W}(\text{CO})_2\text{Cp}$ to give the final product.

V

CONCLUDING REMARKS

The field of transition metal carbyne chemistry has matured to the point where a great deal is known about the structure, bonding, and reactivity of the carbyne ligand. On the other hand, there are some surprising gaps in our knowledge of these complexes. For example, there are no complexes with alkoxycarbyne ($\equiv\text{C-OR}$) ligands. Also the known carbyne complexes involve transition metals toward the left side of the periodic table. Still there are no carbyne complexes of metals in group 9 (Co, Rh, Ir) or 10 (Ni, Pd, Pt). Since these are often catalytic metals, there may be some significance to this observation. However, carbyne complexes of these metals may be found and perhaps be of unusual importance for understanding the homogeneous and heterogeneous catalytic activity of these metals. In any event, it seems certain that carbyne complexes will become more and more common in organotransition metal chemistry.

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The Organic Chemistry of Platinum(IV)

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I

INTRODUCTION

During the last two decades the organic chemistry of platinum has received great impetus in both basic and applied research. In its important oxidation states platinum displays a variety of exciting reactions which are unparalleled. While platinum(II) compounds have proved their potential in biological applications such as in cancer chemotherapy, and in industrial applications as homogeneous catalysts, platinum(IV) complexes have contributed significantly to our knowledge of organometallic chemistry from the isolation of the first alkyl compound of group 8 metals, $[\text{PtMe}_3\text{I}]_4$, by Pope and Peachy (1) in the beginning of the century to the first metallacycloalkane compound, $[\text{Pt}(\text{CH}_2)_3\text{Cl}_2]_n$, discovered by Tipper (2) in 1955.

Platinum, in its compounds, shows a distinct preference for three oxidation states, namely, zero, +2, and +4, although compounds in other oxidation states (+1, +3, etc.) are also known. Oxidative addition and reductive elimination reactions are facile with platinum compounds of the three main oxidation states. These reactions proceed by a two-electron process. The predominant geometry for the +2 oxidation state is square planar, and for the +4 oxidation state it is octahedral.

A review of organoplatinum(IV) compounds was published by Thayer in 1970 (3). In related reviews which have appeared in recent years contextual studies with respect to platinum(IV) compounds have been reported (4–6). Much research and novel advances in the organic chemistry of platinum(IV) have been reported since Thayer's review (3). This article is aimed at bringing out the salient discoveries made recently in the organic chemistry of platinum(IV).

II

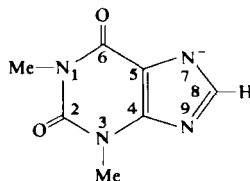
MONOORGANOPLATINUM(IV) COMPOUNDS

Investigations on monoorganoplatinum(IV) compounds are scanty probably because of the absence of straightforward preparative methods, and also because of their poor solubilities in organic solvents. Reaction of PtCl_4 with MeMgI yields mono-, di-, and trimethylplatinum(IV) iodides, depending upon the reaction conditions (7,8). Employing this reaction route, Gilman *et al.* (7) isolated $[\text{PtMeI}_3]$ and salts of $[\text{PtMeI}_5]^{2-}$.

Monoorganoplatinum(IV) compounds are generally prepared by the oxidative addition of halogens to platinum(II) complexes. Thus addition of iodine to $[\text{PtMe(I)L}_2]$ ($\text{L} = \text{Lut}$ or $\text{L}_2 = \text{tetrameen}$)¹ in chloroform gave sparingly soluble platinum(IV) complexes which on prolonged standing in solution lost the methyl group (9). Oxidation of *trans*- $[\text{PtMe(X)(EMe}_2\text{Ph)}_2]$ ($\text{E} = \text{P, As; X} = \text{Cl, Br, I}$) with halogens gave methylplatinum(IV) compounds (10,11). *N*-Bromosuccinimide can also be used in place of bromine in these oxidative addition reactions (12). Halogenation of *cis*- or *trans*- $[\text{PtAr(X)L}_2]$ ($\text{Ar} = \text{Ph, } o\text{-FC}_6\text{H}_4, p\text{-FC}_6\text{H}_4, \text{X} = \text{Cl, L} = \text{PEt}_3$; or $\text{Ar} = \text{C}_6\text{F}_5, \text{X} = \text{Cl, Br, I, L} = \text{PEt}_3, 1/2 [(\text{AsMe}_2)_2\text{C}_6\text{H}_4]$) yields $[\text{PtAr(X)}_3\text{L}_2]$ in which the phosphine ligands ($\text{L} = \text{PEt}_3$) are mutually *trans*. Although $[\text{Pt(Ph)Cl}_3(\text{PEt}_3)_2]$ is inert to chlorine, in the presence of AlCl_3 it gives a product in which aromatic substitution has occurred, $[\text{Pt}(p\text{-ClC}_6\text{H}_4)\text{Cl}_3(\text{PEt}_3)_2]$ (13). In liquid SO_2 at 100°C the latter complex rearranges to afford $[\text{PPhEt}_3][\text{PtCl}_3(\text{PEt}_3)]$ (13).

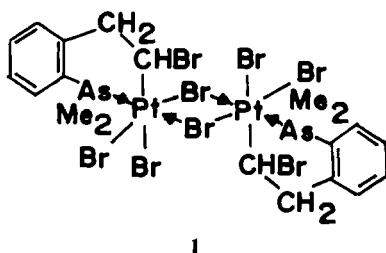
Oxidation of chlorovinylplatinum(II) complexes with stoichiometric amounts of chlorine gives the vinylplatinum(IV) compounds $[\text{Pt}(\text{CX} = \text{CClY})\text{Cl}_3(\text{PMePh}_2)_2]$ ($\text{X, Y} = \text{H; X} = \text{H, Y} = \text{Cl}$). Further reaction of

¹ Abbreviations: py, pyridine; lut, 3,5-lutidine (3,5-dimethylpyridine); gly, glycine ($\text{H}_2\text{-NCH}_2\text{COOH}$); acacH, acetylacetone; SalNR, salicylidineimine ($\text{R} = \text{alkyl or aryl}$); β -thiodik, thio- β -diketone; en, ethylenediamine; tetrameen, tetramethylenediamine; bipy, 2,2'-bipyridyl; phen, 1,10-phenanthroline; dppm, bis(diphenylphosphino)methane; dppe, bis(1,2-diphenylphosphino)ethane; Ox, 8-hydroxyquinolinolate ion; pz $_2$ CH $_2$, bis(1-pyrazolyl)methane; $(\text{Me}_2\text{pz})_2\text{CH}_2$, bis(3,5-dimethyl-1-pyrazolyl)methane; py $_2$ CH $_2$, bis(2-pyridyl)methane; dibm, diisobutylmethane; COD, cycloocta-1,5-diene, thp, theophyllinate,

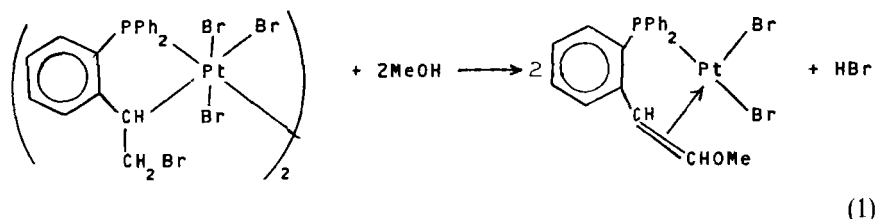


chlorine with $[\text{Pt}(\text{CH}=\text{CCl}_2)\text{Cl}_3(\text{PMePh}_2)_2]$ resulted in the substitution of the vinylic hydrogen atom by chlorine (16).

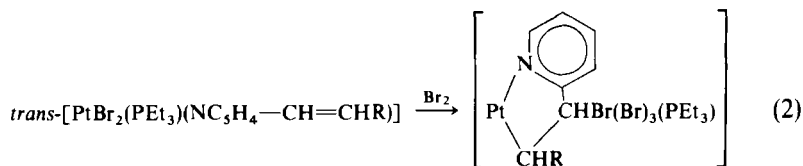
Bromination of platinum(II) complexes having amine, tertiary phosphine, or arsine ligands containing at least one olefinic group often yields metallated platinum(IV) complexes (17–22). Two series of complexes, monomeric from $[\text{PtX}_2\text{L}_2]$ and dimeric from $[\text{PtX}_2\text{L}]_2$, are formed. The platinum–carbon bond in monomeric complexes is cleaved by excess bromine to yield $[\text{Pt}(\text{LBr}_2)\text{Br}_4]$ while the dimeric complexes such as (1) are stable toward

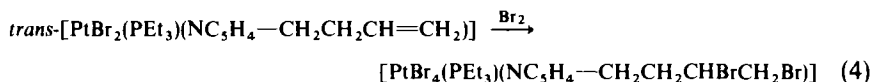
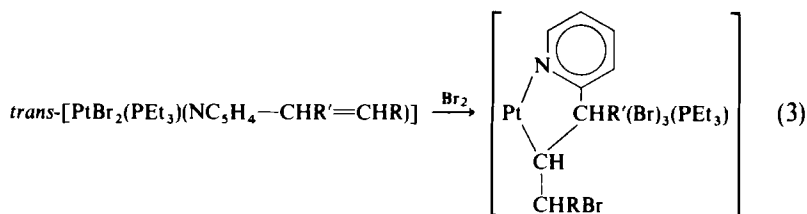


bromine. The monomeric platinum(IV) complexes of the vinyl ligand undergo ring expansion on boiling in water or alcohol (19), while the dimeric complexes react with alcohols [Eq. (1)] to eliminate HBr and give platinum(II) olefinic complexes (17,18).

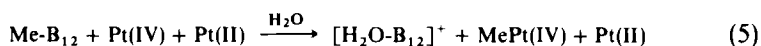


The bromination reactions of 2-(alkenyl)pyridine complexes of platinum(II) (21) have demonstrated that when the olefinic bond is in the 2 or 3 position of the side chain, metallation occurs, whereas when the olefin is in the 4 position no metallation occurs. However, bromine addition to both Pt(II) and the olefin double bond takes place [Eqs. (2)–(4)].





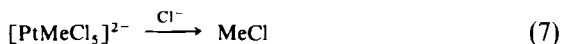
Oxidative addition of alkyl halides (RX , $\text{R} = \text{Me}$, Et ; $\text{X} = \text{I}$) on $[\text{PtCl}_4]^{2-}$ in water yields the monoorganoplatinum(IV) anions, $[\text{PtRCl}_4(\text{H}_2\text{O})]^-$, which have been isolated from solutions as K^+ , Rb^+ , or Cs^+ salts (23–25). Methylcobalamine (Me-B_{12}) slowly methylates $[\text{PtCl}_6]^{2-}$ in the presence of platinum(II) ions giving monomethylplatinum(IV) anions [Eq. (5)] (26–31).



NMR studies (^1H , ^{13}C , and ^{195}Pt) have demonstrated that the methyl group is transferred to Pt(II) which on formal two-electron oxidation generates MePt(IV) with concomitant reduction of the platinum(IV) to Pt(II) . Thus, for methylation to occur salts in both oxidation states must be present [Eq. (6)].

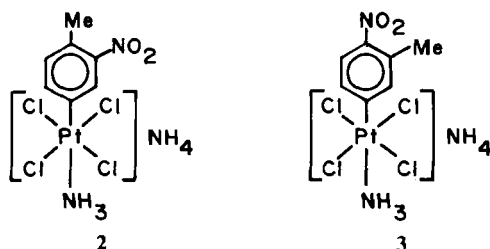


Nucleophilic attack at the methyl carbon of the methylplatinum(IV) anions has been observed [Eqs. (7) and (8)] with loss of the methyl group (23–26).

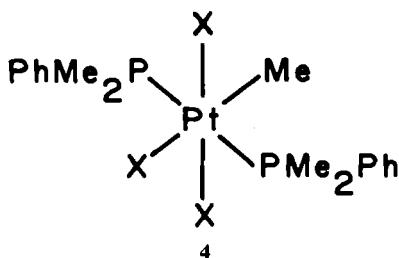


Monoarylplatinum(IV) complexes have been postulated as intermediates in the H_2PtCl_6 -catalyzed chlorination and polymerization of aromatic compounds. Such complexes have been isolated recently by Shul'pin *et al.* (32,33). Benzene or substituted benzenes react with H_2PtCl_6 in $\text{CF}_3\text{COOH}/\text{H}_2\text{O}$ to afford anionic *o*-aryl platinum(IV) complexes which may be isolated as ammonium salts. In the case of monosubstituted benzenes mixtures of meta- and para-platinated isomers have been obtained, and no example of ortho metallation has been observed (32,33). Electron-withdrawing groups in the aromatic ring retard the rate of metallation. *o*-Nitrotoluene gave two isomers (2 and 3).

Pyrolysis of $[\text{PtMe(X)}_3(\text{PMe}_2\text{Ph})_2]$ above 180°C gives MeX and a mixture of *cis*- and *trans*- $[\text{PtX}_2(\text{PMe}_2\text{Ph})_2]$ (34). The low dipole moment (4.3 D) of



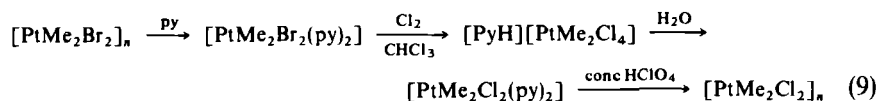
$[\text{PtMe}(\text{X})_3(\text{PMe}_2\text{Ph})_2]$ ($\text{X} = \text{Cl}, \text{Br}$), and the ^1H -NMR spectral data have been interpreted in terms of configuration 4 (10).

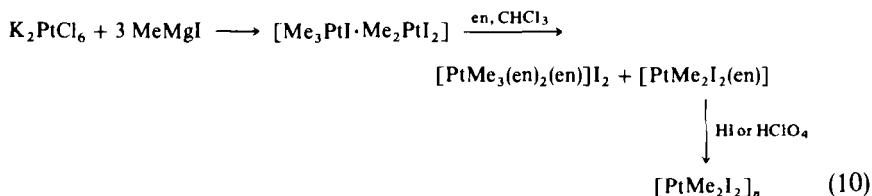


III

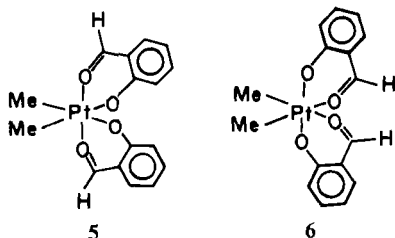
DIORGANOPLATINUM(IV) COMPOUNDS

The first diorgano platinum(IV) compound, $[\text{PtMe}_2\text{I}_2]_n$, was isolated by treating $[\text{PtCl}_6]^{2-}$ with methylmagnesium iodide in diethyl ether (7). Later this product was obtained from the reaction of $[\text{PtMe}_2(\text{COD})]$ with iodine (35). Related diethyl and dibenzoyl complexes have been prepared (35). A less general route to the species $[\text{PtMe}_2\text{X}_2]$ has been discovered. Treatment of $[\text{PtMe}_3\text{I}]_4$ with bromine, in refluxing HBr , affords $[\text{PtMe}_2\text{Br}_2]_n$ (36). The corresponding chloro and iodo complexes have been obtained [Eqs. (9) and (10)]. These halides are highly polymeric, as evidenced by their low solubilities and the presence of both terminal and bridging $\text{Pt}-\text{X}$ stretching frequencies in the infrared spectra (36,37). They react with neutral donor ligands to give mononuclear complexes of the type $[\text{PtMe}_2(\text{X})_2\text{L}_2]$ (37).



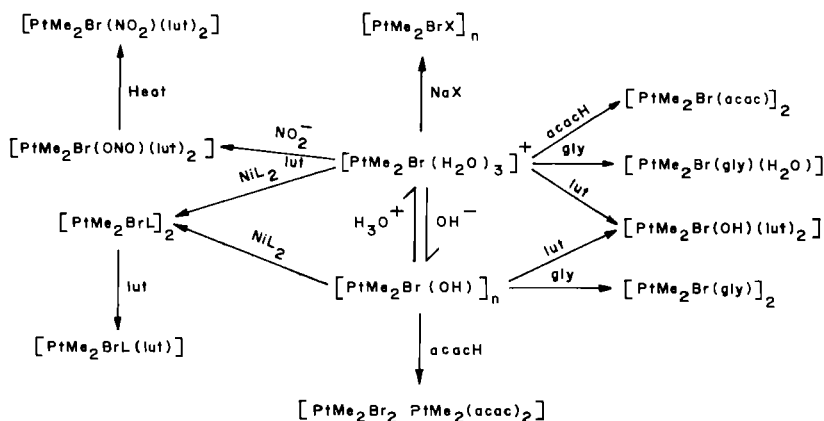


The $[\text{PtMe}_2\text{Br}_2]_n$ complex dissolves in hot concentrated sodium hydroxide solution to produce $[\text{PtMe}_2(\text{OH})_4]^{2-}$, which on neutralization with perchloric acid affords a fine white precipitate, $[\text{PtMe}_2(\text{OH})_2(\text{H}_2\text{O})_2]$ (38). The latter complex is considered to be polymeric with bridging OH groups. It reacts with NaX ($\text{X} = \text{Cl}, \text{Br}, \text{SCN}$) to produce $[\text{PtMe}_2\text{X}_4]^{2-}$, and with NaNO_2 yields $[\text{PtMe}_2(\text{ONO})_2(\text{NO}_2)_2]^{2-}$. The latter with lut gives $[\text{PtMe}_2(\text{ONO})_2(\text{lut})_2]$ (38). Both hydroxy species are useful starting materials for the preparation of a range of dimethylplatinum(IV) compounds since they react with weak acids such as β -diketones and salicylaldehyde (38,39). The salicylaldehydato complex shows a relatively large ^{195}Pt coupling to the aldehydic proton in the ^1H -NMR spectrum. Initially isomer **5** forms, but on heating in high boiling solvents it converts to another isomer (**6**). Both isomers



(**5** and **6**) react with primary amines to produce salicylidineimine complexes (39). A direct method for the synthesis of salicylidineimine complexes by treating of $[\text{PtMe}_2\text{X}_2]_n$ ($\text{X} = \text{Cl}, \text{Br}$) with *N*-organosalicylidineimines (via the thallium complex) yielded octahedral anionic complexes $[\text{M}][\text{PtMe}_2(\text{X})_2(\text{SalNR})]$ ($\text{R} = \text{Me}, \text{Ph}, \text{c-Hx}$) rather than $[\text{PtMe}_2(\text{SalNR})_2]_2$ (40).

Reaction of $[\text{PtMe}_2\text{Br}_2]_n$ with 1 equivalent of a silver salt (AgNO_3 or AgClO_4) in water yields an acidic solution which contains the $[\text{PtMe}_2(\text{Br})(\text{H}_2\text{O})_3]^+$ ion. Although this cationic complex cannot be isolated, on neutralization it yields $[\text{PtMe}_2(\text{Br})(\text{OH})]_n$ in which the platinum atoms are bridged through hydroxy bridges (41,42). The latter in methanol gives dimeric $[\text{PtMe}_2(\text{Br})(\text{OH})(\text{MeOH})]_2$, whereas a different dimeric anionic complex, $[\text{PtMe}_2(\text{Br})(\mu\text{-OH})(\text{OH})]_2^{2-}$, is formed in aqueous KOH at pH 9. These complexes have been studied by ^{13}C - and ^{195}Pt -NMR spectroscopy, and it has been observed that the ^{195}Pt resonances for hydroxy-bridged complexes

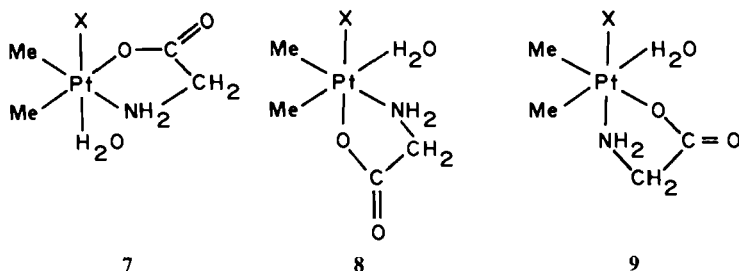


(L = $SalNR$ or β -THIODIK ; X = Cl, Br, SCN)

SCHEME 1

appear at lower field than those of the monomeric complexes (43). The complexes $[PtMe_2(Br)(H_2O)_3]^+$ and $[PtMe_2(Br)(OH)]_n$ react with various neutral and anionic ligands (41,42,44). Some of their reactions are shown in Scheme 1.

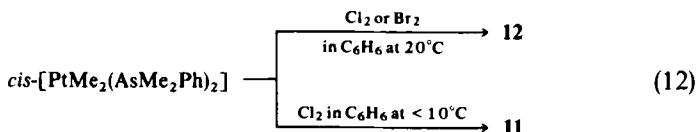
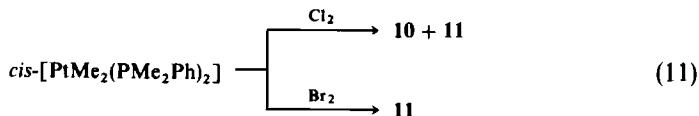
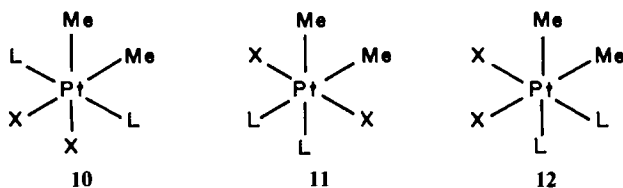
Reaction with glycine affords $[PtMe_2(Br)(gly)(H_2O)]$ which exists as three geometrical isomers (7–9), each form having the two methyl groups and the ligand X in mutually cis positions (44,45). The isomers containing a water



molecule trans to a methyl group are labile and crystallize from the solution as $[PtMe_2(X)(gly)]_2$ (X = Br) species. The latter complex also exists in three geometrical forms (both N atoms cis or trans to methyl groups and one N atom trans to methyl), all of which have been isolated (46). All three isomers of $[PtMe_2(X)(gly)(H_2O)]$ react with sodium glycinate to yield $[PtMe_2(X)(gly)(OH)]^-$, $[PtMe_2(X)(gly)_2]^-$, and $[PtMe_2(X)(gly)_3]^{2-}$, respectively, depending on the stoichiometry of the reactants and the stereochemistry of the

starting platinum complex (46). Alkaline solutions of $[\text{PtMe}_2(\text{Br})(\text{gly})(\text{OH})]^-$ on heating yield $[\text{PtMe}_2(\text{OH})(\mu\text{-NHCH}_2\text{COO})_2]^{2-}$ in which deprotonated glycine is acting as an amide bridging ligand (47). Protonation of $\text{Pt}-\text{OH}$ to $\text{Pt}-\text{OH}_2$ takes place on acidifying the above solution from which $[\text{PtMe}_2(\text{gly})(\text{H}_2\text{O})_2]^+$ (N atom trans to H_2O) is obtained.

Another important method for synthesizing diorganoplatinum(IV) complexes involves the oxidative addition reaction of halogens or RX on corresponding platinum(II) complexes. Thus, dimethylplatinum(IV) complexes containing tertiary phosphines or arsines have been prepared either by the addition of halogens to $[\text{PtMe}_2(\text{L})_2]$ or by the reaction of RX with $[\text{PtMe}(\text{X})(\text{L})_2]$ ($\text{L} = \text{PMe}_2\text{Ph}$, AsMe_2Ph) (10,11). The nature of the reactants and reaction conditions have profound influence on the stereochemistry of the products (10–12), as shown in Eqs. (11) and (12).



The complex $\text{cis-}[\text{PtMe}_2(\text{PMe}_2\text{Ph})_2]$ can also be halogenated by *N*-bromosuccinimide or 2-nitrophenylsulfonyl chloride to give $[\text{PtMe}_2(\text{X})_2(\text{PMe}_2\text{Ph})_2]$ (12). Dialkylbis(phosphine)platinum(II) complexes are readily oxidized by hexachloroiridate(IV) to afford two types of product, depending on the nature of the alkyl group and the tertiary phosphine (48). Thus $\text{cis-}[\text{PtMe}_2(\text{PMe}_2\text{Ph})_2]$ gives $[\text{PtMe}_2(\text{X})_2(\text{PMe}_2\text{Ph})_2]$, while the analogous triphenylphosphine complex yields both $[\text{PtMe}_2(\text{X})_2(\text{PPh}_3)_2]$ and $[\text{PtMe}(\text{X})(\text{PPh}_3)_2]$. The diethylplatinum(II) complexes $\text{cis-}[\text{PtEt}_2(\text{PR}_3)_2]$ ($\text{PR}_3 = \text{PMe}_2\text{Ph}$, PPh_3), on the other hand, lose one ethyl group as EtCl and yield only platinum(II) complexes $[\text{PtEt}(\text{PR}_3)_2\text{S}]^+$ ($\text{S} = \text{MeCN}$) (48).

Diorganoplatinum(IV) complexes containing nitrogen donor ligands have also been prepared by oxidative addition reactions involving X_2 or RX and

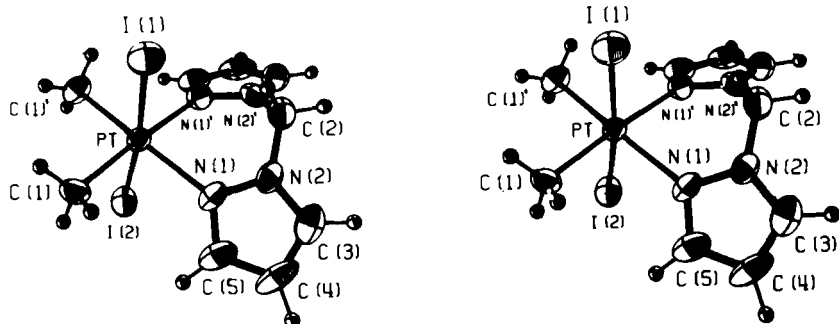


FIG. 1. Stereoview of $[\text{PtMe}_2\text{I}_2(\text{pz}_2\text{CH}_2)]$. [Reprinted with permission from *Organometallics* **2**, 806. Copyright (1983) American Chemical Society (49).]

platinum(II) complexes. Addition of methyl iodide to $[\text{PtMe}(\text{I})(\text{L})_2]$ ($\text{L} = \text{lut}$ or $\text{L}_2 = \text{tetrameen}$) affords the platinum(IV) complexes, $[\text{PtMe}_2(\text{I})_2\text{L}_2]$ (9). Treatment of $[\text{PtMe}_2(\text{COD})]$ with iodine, in presence of chelating nitrogen ligands, $\widehat{\text{NN}}$ [$\widehat{\text{NN}} = \text{pz}_2\text{CH}_2$, $(\text{Me}_2\text{pz})_2\text{CH}_2$, py_2CH_2 , bipy] gives the platinum(IV) complexes, $[\text{PtMe}_2\text{I}_2(\widehat{\text{NN}})]$ (49). The molecular structures of $[\text{PtMe}_2\text{I}_2(\text{pz}_2\text{CH}_2)]$ and $\{\text{PtMe}_2\text{I}_2[(\text{Me}_2\text{pz})_2\text{CH}_2]\}$ have been determined by X-ray diffraction. In both molecules platinum has an octahedral geometry, with methyl groups trans to the $\widehat{\text{NN}}$ ligand and iodide ligands occupying the axial positions (49). The six-membered ring has essentially the boat conformation, and the individual pyrazolyl rings are planar in both molecules (Figs. 1 and 2). Crystallographic data for organoplatinum(IV) compounds are listed in Table I.

Oxidative addition reactions have also been employed to synthesize diarylplatinum(IV) complexes (14,15,50–53). The ^1H - and ^{19}F -NMR spectra of pentafluorophenyl complexes have been reported, and it has been concluded that, at low temperatures, rotation of the phosphine ligands is

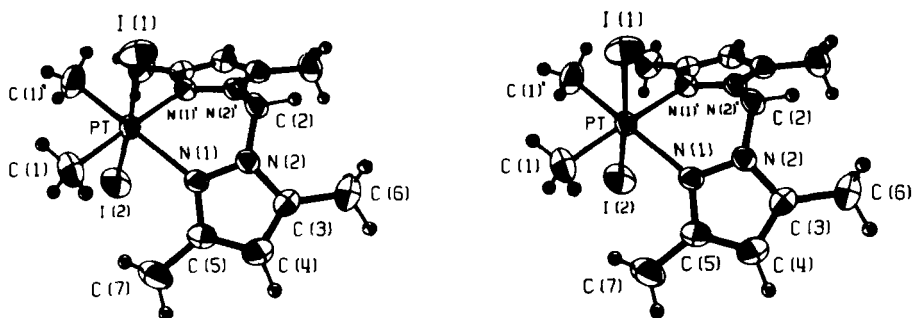


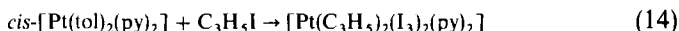
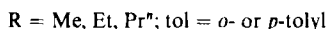
FIG. 2. Stereoview of $\{\text{PtMe}_2\text{I}_2[(\text{Me}_2\text{pz})_2\text{CH}_2]\}$. [Reprinted with permission from *Organometallics* **2**, 806. Copyright (1983) [American Chemical Society (49).]

TABLE I
CRYSTALLOGRAPHIC DATA FOR ORGANOPLATINUM(IV) COMPOUNDS

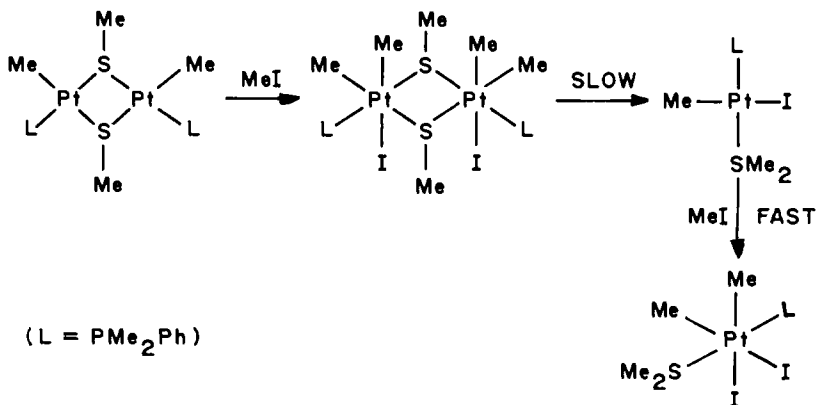
Compound	Unit cell	Space group	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	z	Reference
[PtMe ₂ I ₂ (pz ₂ CH ₂)]	Orthorhombic	<i>Pnma</i>	8.218(2)	13.146(2)	13.453(2)	—	—	—	4	49
{PtMe ₂ I ₂ [(Me ₂ pz) ₂ CH ₂]}	Monoclinic	<i>P2</i> ₁ / <i>m</i>	7.420(1)	14.426(3)	8.686(1)	—	100.90(1)	—	2	49
[PtMe ₂ (NO ₂) ₂ (PEt ₃) ₂]	Monoclinic	<i>P2</i> ₁	7.278(1)	12.120(1)	11.867(1)	—	94.56	—	2	61
[PtMe ₂ (OOPr ^t)I(phen)]	Monoclinic	<i>P2</i> ₁ / <i>n</i>	9.946(2)	11.340(3)	16.374(2)	—	94.55	—	4	129
[PtMe ₃ Cl] ₄	Cubic	<i>T_d</i> ³ – <i>I</i> _{43m}	10.55	—	—	—	—	—	8	86
[PtMe ₃ I] ₄	Monoclinic	<i>P2</i> ₁ / <i>a</i>	17.77	19.39	17.12	—	115.41	—	2	165
[PtMe ₃ OH] ₄	Cubic	<i>I</i> _{43m} or <i>I</i> _{m3m}	10.14	—	—	—	—	—	2	161
[PtMe ₃ N ₃] ₄	—	<i>P3</i> ¹ <i>c</i> <i>1</i>	10.08	—	31.49	—	—	—	4	166
[PtEt ₃ Cl] ₄	Monoclinic	<i>P2</i> ₁ / <i>n</i>	16.65	12.08	17.00	—	90.5	—	4	163
{PtMe ₃ [(Me ₂ pz) ₂ CH ₂]}	Orthorhombic	<i>Pcmm</i>	11.936(5)	14.462(4)	10.138(5)	—	—	—	4	96
[PtMe ₃ I(PhMeAsCH ₂ CH ₂ AsPhMe)]	Monoclinic	<i>P2</i> ₁ / <i>c</i>	17.008	15.736	8.393	—	101.37	—	4	157
[Pt ₂ Me ₃ L(μ-I)(μ-dmpm)] ₂ ⁺ [L = 1/2(I + Me); dmpm = (Me ₂ P) ₂ CH ₂]	Triclinic	<i>P1</i> ¹	9.240(2)	9.328(4)	18.044(7)	107.39(4)	94.63(3)	96.93(3)	2	132
[Pt ₂ Me ₄ Br ₂ (μ-CH ₂ C ₆ H ₄ CH ₂)(dppm)]	Orthorhombic	<i>P2</i> ₁ 2 ₁ 2 ₁	10.481(3)	17.694(5)	18.842(7)	—	—	—	4	167
[(PtMe ₃ Br) ₂ (MeSeSeMe)]	Orthorhombic	<i>P2</i> ₁ 2 ₁ 2 ₁	9.358(1)	12.425(2)	14.977(3)	—	—	—	4	103
[(PtMe ₃ I) ₂ (Me ₂ CCH ₂ SeSeCH ₂)]	Monoclinic	<i>P2</i> ₁ / <i>n</i>	9.519(3)	13.317(4)	16.182(5)	—	94.28(3)	—	4	115

$[(\text{PtMe}_3\text{Cl})_2(\text{SCH}_2\text{SCH}_2\text{SCH}_2)]$	Monoclinic	$P2_1/c$	9.872(1)	14.289(2)	12.951(2)	—	106.83(1)	—	4	107
$[(\text{PtMe}_3\text{Cl})_2(\text{SCH}_2\text{SCH}_2\text{SCH}_2\text{SCH}_2)]$	Triclinic	$P\bar{1}$	10.344(2)	11.915(4)	12.758(3)	132.42(2)	91.16(2)	113.50(2)	2	116
$[\text{PtMe}_3\text{Ox}]_2$	Orthorhombic	$P2_12_12_1$	15.23	16.09	9.48	—	—	—	8	160
$[\text{PtMe}_3(o\text{-OC}_6\text{H}_4\text{CHO})]_2$	Triclinic	$P\bar{1}$	10.828(5)	11.455(5)	9.147(5)	74.7(5)	110.8(5)	92.55(5)	4	158
$[\text{PtMe}_3\text{Cp}]$	Orthorhombic	$Pna2_1$	11.631	7.180	10.359	—	—	—	4	191
$[\text{PtMe}_3(\text{Pr}^n\text{COCHCOPr}^n)]_2$	Monoclinic	$P2_1/a$	17.71(3)	10.55(2)	9.15(1)	—	102.8(2)	—	—	196
$[\text{PtMe}_3(\text{MeCOCHCOOEt})]_2$	Monoclinic	$P2_1/c$	8.83(2)	14.12(5)	9.30(2)	—	95.00(25)	—	—	208
$[\text{PtMe}_3(\text{acac})(\text{bip})]$	Monoclinic	$P2_1/c$	14.863(5)	8.480(3)	13.749(5)	—	99.24(4)	—	4	217
$[(\text{PtMe}_3\text{acac})_2\text{en}]$	Monoclinic	$I2/a$	23.19(3)	6.46(1)	16.42(2)	—	103.0(3)	—	4	218
$[\text{Pt}(\text{CH}_2)_3\text{Cl}_2(\text{py})_2]$	Monoclinic	$P2_1/c$	13.37	13.11	8.40	—	91.1	—	4	252
$[\text{Pt}(\text{CH}_2)_3\text{Cl}_2(\text{bipy})]$	Orthorhombic	$Amma$	12.414(12)	7.683(7)	14.583(15)	—	—	—	4	260
$[\text{Pt}(\text{C}_3\text{H}_4\text{Ph}_2)\text{Cl}_2(\text{py})_2] \cdot 1/2\text{EtOH}$	Triclinic	$P\bar{1}$	13.148(6)	14.052(7)	17.860(8)	62.53(1)	108.25(3)	114.69(3)	4	267
$\{\text{Pt}[\text{CH}_2\text{C}(\text{Me})(\text{CH}_2\text{OH})\text{CH}_2]\text{Cl}_2(\text{py})_2\}$	Orthorhombic	$D_{2h}^{15}Pbca$	19.596(7)	13.893(5)	13.108(5)	—	—	—	8	266
$[\text{Pt}(\text{CH}_2)_4\text{I}_2(\text{PMe}_2\text{Ph})_2]$	Monoclinic	$C2/c$	15.286	9.709	17.036	—	107.49	—	4	239
$[\text{Pt}(\text{CEt})(\text{pyH})\text{Cl}_4(\text{py})]$	Monoclinic	$P2_1/c$	9.263(15)	14.24(2)	16.78(3)	—	94.1	—	4	253
$\{\text{Pt}[\text{C}(4\text{-ClC}_6\text{H}_3\text{NH})(\text{NHMe})]\text{Cl}_2(\text{PEt}_3)_2\}\text{ClO}_4$	Monoclinic	$P2_1/a$	13.451(2)	21.381(5)	13.368(2)	—	130.73(1)	—	4	277

prevented by steric interaction with *cis*-pentafluorophenyl groups (14). The reaction of alkyl iodides with *cis*-[Pt(tol)₂(py)₂] is accompanied by displacement of a tolyl group (54,55) and formation of diorganoplatinum(IV) complexes [Eq. (13)]. A similar reaction with allyl iodide gave a platinum(IV) complex with triiodide ligands (55), and in which the allyl groups are σ -bonded [Eq. (14)].



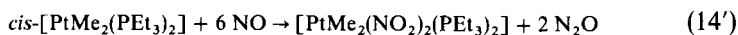
The reaction of methyl iodide with the mercapto-bridged dinuclear platinum(II) complexes, [Pt(μ -SMe)R(PMe₂Ph)]₂ (R = Me, Ph), involves dinuclear platinum(IV) intermediates which ultimately yield mononuclear platinum(II) or (IV) complexes, depending on the nature of R (56,57). When R is phenyl mononuclear platinum(II) complexes, [PtPh(I)(SMeR)(PMe₂Ph)] (R = Me, CD₃), are obtained, while when R is Me the platinum(IV) complex [PtMe₂(I)₂(PMe₂Ph)(SMe₂)] is formed according to the following reaction sequence:



Alcohols and water add oxidatively to [PtMe₂L] (L = bipy or phen) to give cationic platinum(IV) complexes, [PtMe₂(OR)L(H₂O)]⁺ (R = H, Me, Et, Prⁱ), which were isolated as salts of bulky anions, such as PF₆⁻, BPh₄⁻, or ClO₄⁻ (58,59). The alkoxy-platinum(IV) bond is inert to solvolysis with alcohols, water, or dilute HClO₄.

The mono- and dioxides of nitrogen oxidize platinum(II) complexes to platinum(IV) (60,61). Thus, reaction of NO or NO₂ with *cis*-[PtMe₂(PR₃)₂] (PR₃ = PEt₃, PMe₂Ph) affords dimethylplatinum(IV) complexes, [PtMe₂(X)₂(PR₃)₂] (X = NO₂, PR₃ = PEt₃, PMe₂Ph; X = NO₃, PR₃ = PMe₂Ph).

Nitric oxide gives initially the *cis,cis,cis* isomer (**12**: L = PMe₂Ph; X = NO₂) which slowly isomerizes in solution to the more stable isomer **10** (L = PMe₂Ph; X = NO₂) (69). However, when L is PEt₃, only complex **10** (L = PEt₃; X = NO₂) could be isolated. Its structure was confirmed by X-ray structural analysis (61). The reaction of NO with dimethyl bis(triethylphosphine)-platinum(II) was thought to proceed as shown in Eq. (14').

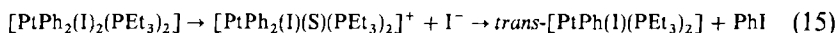


Nitrous oxide was the only gaseous product formed during the reaction (61). However, formation of dinitrogen has been proposed by Puddephatt and Thompson (60). Interestingly, when a reaction mixture consisting of *cis*-[PtMe₂(PMe₂Ph)₂] and NO was allowed to stand for a long time, equimolar mixtures of *fac*-[PtMe₃(NO₂)(PMe₂Ph)₂] and *trans*-[PtMe(NO₂)(PMe₂Ph)₂] were formed. Formation of these products involves a methyl group transfer reaction from [PtMe₂(PMe₂Ph)₂] to [PtMe₂(NO₂)₂(PMe₂Ph)₂]. In general, methyl group transfer from Pt(II) to Pt(IV) is complex, yet the reaction occurs readily. Loss of phosphine from isomer **11**, promoted by the high *trans* influence of the methyl group, is believed to be the initial process involved in such reactions (60,62,63). Thus, isomer **11** (*trans,cis,cis*) gives trimethylplatinum(IV) complexes, while isomer **10** (*cis,cis,trans*) is inert toward dimethylplatinum(II) complexes (L = PMe₂Ph; X = I).

Group 4B metal alkyl halides or HgX₂ oxidatively add to platinum(II) complexes to give the corresponding platinum(IV) derivatives (64–67). Treatment of [PtMe₂(bipy)] with organogermanium, -tin, and -lead halides gives complexes of the type [PtMe₂X(ER_nCl_{3-n})(bipy)] (E = Ge, Sn, Pb). The stability of the product is dependent on the nature of the Group 4B element rather than on the alkyl group. The complexes [PtMe₂(X)(HgX)(bipy)] (X = Cl, Br, I, OAc, CF₃COO) are obtained from [PtMe₂(L—L)] and HgX₂ (65) in equimolar amounts. Treatment of [PtMe₂(bipy)] with 4 equivalents of Hg(OOCCF₃)₂ gives [Pt₄Me₃(OOCCF₃)(HgOOCCF₃)(bipy)₄] (67).

The stoichiometric reaction of AgPF₆ with [PtMe₂I₂(PMe₂Ph)₂], in the presence of certain ligands, gives salts of composition [PtMe₂(I)-(PMe₂Ph)₂L][PF₆]₂ and [PtMe₂(PMe₂Ph)₂(L)₂][PF₆]₂ [L = py, EtNC, PMe₂Ph, MeCN, P(OMe)₃; L—L = Diphos, diars, bipy] (68). The observed variations in ²J(Pt—H) in the ¹H-NMR spectra of these complexes have been used as a quantitative measure of the *trans* influence for a series of neutral donor ligands.

Reductive elimination reactions of diorganoplatinum(IV) compounds have been studied (34,49,69). The complex [PtPh₂(I)₂(PEt₃)₂] reductively eliminates iodobenzene in methanol (69). The first step in the reaction involves reversible dissociation of the iodide ligand, followed by unimolecular reduction of the cationic platinum(IV) complex [Eq. (15)].



S = solvent

Pyrolysis of dimethylplatinum(IV) compounds yields methyl halide or ethane depending on the configuration of the complex (34,49). Complexes with configuration **10** give mainly or completely methyl halide, while those with configuration **11** give mainly ethane. However, complexes containing AsMe_2Ph ligands give a mixture of methyl halide and ethane (34). The UV photolysis of methylplatinum(IV) compounds involves free radicals (70).

IV

TRIORGANOPLATINUM(IV) COMPOUNDS

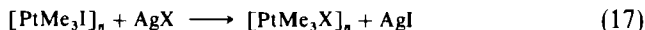
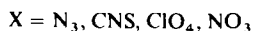
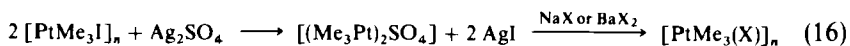
A. Halides, Pseudohalides, and Related Compounds

Halides, pseudohalides, and related compounds are among the best known organoplatinum(IV) derivatives, and they have been investigated in great detail. The complex $[\text{PtMe}_3\text{I}]_4$ was the first organoplatinum(IV) compound to be prepared (1907) (1). It was obtained by treating PtCl_4 with MeMgI and has been used as a starting material for the preparation of a number of other trimethylplatinum(IV) complexes. Although the reaction of MeMgI with platinum(IV) halides in diethyl ether or diethyl ether–benzene mixtures produces a mixture of methylplatinum(IV) iodides, namely, $[\text{PtMeI}_3]_n$, $[\text{PtMe}_2\text{I}_2]_n$, $[\text{Me}_3\text{PtI} \cdot \text{Me}_2\text{PtI}_2]$, $[\text{PtMe}_3\text{I}]_2$, and $[\text{PtMe}_3\text{I}]_4$ (7,8), this is the most useful method for the preparation of $[\text{PtMe}_3\text{I}]_4$ (8,71–74). Moreover, as the molar ratio of MeMgI increases from 2 to 15 or 20 mol the total yield of $[\text{PtMe}_3\text{I}]_n$ rises from 12 to 86% (8,74). The yields are also solvent dependent, falling considerably when the mole fraction of ether is raised (8,74). The trimethylplatinum(IV) iodide has been isolated in yellow and white crystalline forms, and both show molecular association corresponding approximately to a tetramer. Their chemical and spectroscopic properties were identical (73). The yellow form is thought to contain some impurities, possibly iodine.

The trimethylplatinum(IV) chloride and bromide have been prepared by treating bis(trimethylplatinum)sulfate (obtained from $[\text{PtMe}_3\text{I}]_4$ and Ag_2SO_4) with KCl and KBr , respectively (75). Trimethylplatinum(IV) chloride can also be obtained from the reaction of K_2PtCl_6 with excess methyl lithium in diethyl ether (76). Reaction of R_2Hg ($\text{R} = \text{Me}, \text{Et}$) with PtCl_4 in acetone gives the corresponding trialkylplatinum(IV) chlorides (77).

Trimethylplatinum(IV) pseudohalides are generally prepared either from the reactions of bis(trimethylplatinum)sulfate with alkali or alkaline earth

metal salts [Eq. (16)] (73,76,78–80) or from treating trimethylplatinum iodide with silver pseudohalides [Eq. (17)] (80,81). Trimethylplatinum salts,



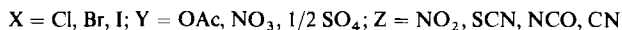
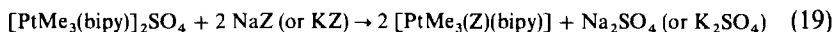
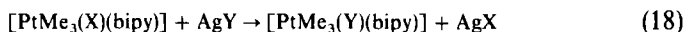
$[\text{PtMe}_3\text{X}]$ ($\text{X} = \text{ClO}_4, \text{NO}_3, \text{SO}_4, \text{OAc}, \text{OOCH}$, phosphate), have been obtained by dissolving $[\text{PtMe}_3(\text{acac})]_2$ in appropriate dilute acid with a little hydrogen peroxide (82,83). Mixed hydroxy-iodo-bridged complexes, $[\text{Pt}_4\text{Me}_{12}\text{I}_{4-n}(\text{OH})_n]$ ($n = 1-4$), have been prepared by treating $(\text{Me}_3\text{Pt})_2\text{SO}_4$ in water with a mixture of NaOH and NaI in the appropriate molar ratio (84). It is interesting to note that in spite of a number of claims (7,85,86) no authentic samples of $[\text{PtMe}_4]$ have yet been reported. Thus the reaction of $[\text{PtMe}_3\text{I}]_n$ with methylsodium, which was thought to afford $[\text{PtMe}_4]$, has been shown to give only $[\text{PtMe}_3(\text{OH})]_n$ (87,88). The reaction of trimethylplatinum hydroxide with mercaptans gives tetrameric trimethylplatinum(IV) mercaptides, $[\text{PtMe}_3(\text{SR})]_4$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^i, \text{CH}_2\text{Ph}, \text{Ph}$) (89,90).

Trimethylplatinum halides and pseudohalides are tetrameric in the solid state as well as in solution. Pseudohalides generally give aqua species, $[\text{PtMe}_3(\text{H}_2\text{O})_3]^+$, in aqueous solutions. Trimethylplatinum nitrate and sulfate are 1:1 and 1:2 electrolytes, respectively (73). Trimethylplatinum perchlorate explodes on heating and also on shock treatment (81). Trimethylplatinum azide on treatment with trimethylphosphite gives *cis*- $\{\text{PtMe}_2\text{-P(OMe)}_3\}_2$ and MeN_3 (91).

B. Complexes with Group 5 and 6 Donor Ligands

Trimethylplatinum halides and pseudohalides react with neutral donor ligands to afford six-coordinate octahedral complexes of the type $[\text{PtMe}_3(\text{X})\text{L}_2]$ (81,92–96). Treatment of $[\text{PtMe}_3\text{I}]_4$ with excess pyridine or 3,5-lutidine gives $[\text{PtMe}_3(\text{I})\text{L}_2]$ ($\text{L} = \text{py}$ or lut) (92,93,95). However, reaction with 1 equivalent of pyridine or treatment of $[\text{PtMe}_3(\text{I})(\text{py})_2]$ with dilute mineral acid yields dimeric platinum species, $[\text{PtMe}_3(\text{I})(\text{py})_2]_2$ (94,95). The dimeric salts $[\text{PtMe}_3(\text{X})(\text{py})_2]_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) may also be obtained by heating the monomers $[\text{PtMe}_3(\text{X})(\text{py})_2]$ (97). Reaction of excess ammonia or methylamine with $[\text{PtMe}_3\text{X}]_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) affords ionic complexes, $[\text{PtMe}_3(\text{am})_3]\text{X}$ (71,95,98–100). The complex $[\text{PtMe}_3(\text{NH}_3)_3]\text{I}$ releases 1 mol of ammonia above 76°C to give $[\text{PtMe}_3(\text{I})(\text{NH}_3)_2]$, which on further heating yields $[\text{PtMe}_3(\text{I})(\text{NH}_3)]_2$, and finally $[\text{PtMe}_3\text{I}]_4$ at 165°C (95,97).

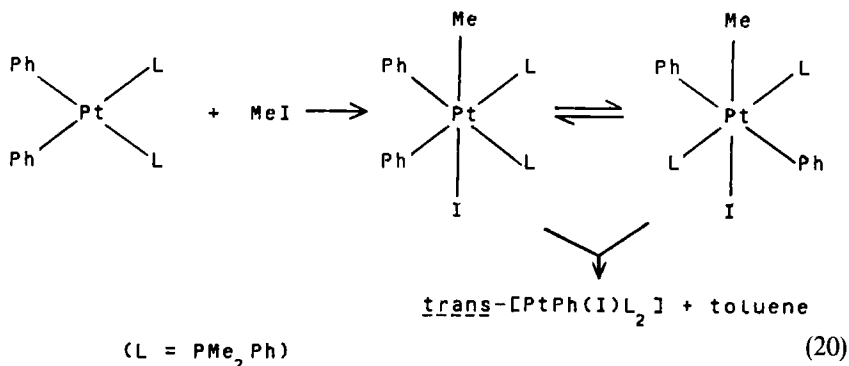
Halides in trimethylplatinum(IV) complexes have been replaced by other anionic ligands as shown in Eqs. (18) and (19) (101).

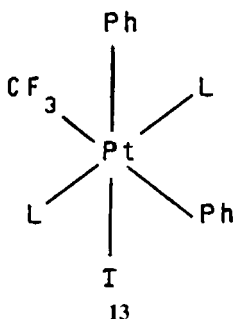


Bi- or polydentate chalcogen ligands react with trimethylplatinum halides to give two series of complexes: $\{[\text{PtMe}_3(\text{X})]_2\text{LL}\}$ [$\text{LL} = \text{Me}-\text{S}-\text{S}-\text{Me}$, $\text{MeSe}-\text{SeMe}$, $\text{MeE}(\text{CHR})\text{EMe}$ ($\text{E} = \text{S, Se}$), $\text{MeS}-\text{CH}_2\text{SMe}$] and $[\text{PtMe}_3(\text{X})\text{LL}]$ [$\text{LL} = \text{MeE}(\text{CH}_2)_n\text{EMe}$ ($n = 2, 3$), $(\text{MeS})_2\text{C}=\text{C}(\text{SMe})_2$, $o\text{-(SMe)}_2\text{-C}_6\text{H}_4$] (102–117). These complexes have been investigated extensively, and the chalcogen inversion has been studied by $^1\text{H-NMR}$ spectroscopy.

Another method for the preparation of triorganoplatinum(IV) compounds involves oxidative addition of alkyl or acyl halides to diorganoplatinum(II) complexes, and this route has been extensively used (10,11,118). Treatment of dimethylplatinum(II) compounds containing tertiary phosphine or arsine ligands with excess methyl halide or acyl halide gives the corresponding triorganoplatinum(IV) complexes, $[\text{PtMe}_2(\text{R})(\text{X})\text{L}_2]$ ($\text{R} = \text{Me, Ac}$; $\text{X} = \text{Cl, Br, I}$; $\text{L} = \text{PMe}_2\text{Ph, AsMe}_2\text{Ph}$) (10,11). Complexes $[\text{PtMe}_3(\text{X})(\text{diars})]$ containing chelating diarsine ligands [$\text{diars} = o\text{-(Me}_2\text{As)}_2\text{C}_6\text{H}_4$ or *rac*- or *meso*- $\text{PhMeAsCH}_2\text{CH}_2\text{AsMePh}$] have also been prepared employing this reaction route (119,120). Acetyl chloride gives *trans* adducts while allyl chloride affords *cis* adducts. Additions on $[\text{PtMe}_2(\text{meso-diars})]$ are stereospecific in all cases (119,120).

Diphenylplatinum(II) compounds react slowly with excess of methyl iodide to give the complexes *trans*- $[\text{PtPh}(\text{I})\text{L}_2]$ via unstable platinum(IV) intermediates, the latter being detected by NMR spectroscopy [Eq. (20)] (121). However, when the reaction is carried out with perfluoroiodomethane, complex 13 is isolated (121), probably formed via isomerization of the initial *trans* addition product. Perfluoroalkyl iodides, in general, oxidatively

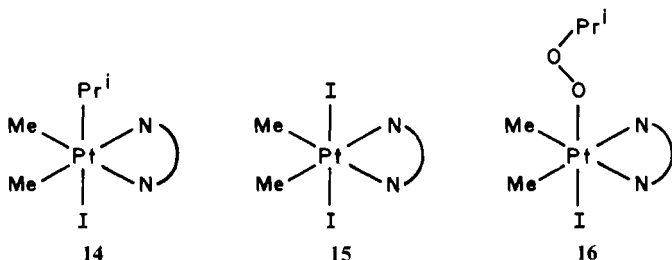




add to platinum(II) compounds to give the trans addition products $[\text{PtMe}_2(\text{R})(\text{I})(\text{L})_2]$ [$\text{R} = \text{CF}_3$, C_2F_5 , C_3F_7 , $(\text{CF}_2)_6\text{CF}_3$; $\text{L} = \text{PMe}_2\text{Ph}$, AsMe_2Ph] (122,123).

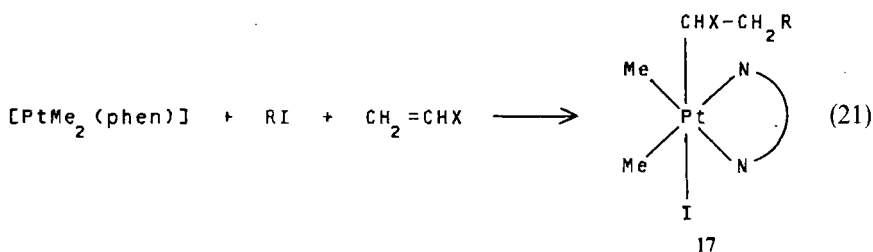
The kinetics of the oxidative addition of MeI or AcCl to *cis*- $[\text{PtMe}_2-(p\text{-CNC}_6\text{H}_4\text{Me})_2]$ has been investigated with chloroform as solvent. The reaction gives exclusively the trans adduct, and the reaction rates obey second-order kinetics. An Arrhenius plot of the kinetic data gives activation energies of 8.6 and 8.5 kcal/mol for the addition of MeI and AcCl , respectively (121). Similar reactions with the phosphine or arsine complexes, $[\text{PtMe}_2\text{L}_2]$ ($\text{L} = \text{PMe}_2\text{Ph}$, AsMe_2Ph), are faster than for the isocyanide complex. These low activation energies are indicative of high electron density on platinum (121). Involvement of a polar transition state has been suggested in these reactions (121,124). Deuterium labeling studies demonstrated that trans addition of alkyl halides on *cis*-diorganoplatinum(II) complexes takes place (125).

Oxidative addition of alkyl halides on diorganoplatinum(II) compounds containing nitrogen donor ligands such as bipy or phen (124,126–129) generally produces trans addition products. The rate of reaction depends on solvent polarity, and the rate increases in polar solvents. A mechanism involving a polar transition state has been suggested (124). The reaction of isopropyl iodide with $[\text{PtMe}_2(\text{phen})]$, however, yields a mixture of three complexes (14–16) under aerobic conditions, while under anaerobic

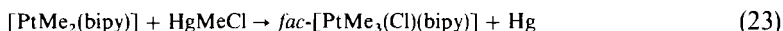
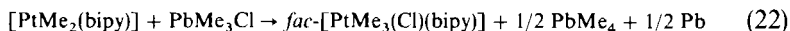


conditions only the trans addition product (**14**) is formed. The rate of reaction of isopropyl iodide with $[\text{PtMe}_2(\text{phen})]$ is independent of oxygen concentration, indicating that oxygen is not involved in a rate-determining step (129).

A free radical mechanism involving a peroxy radical RO_2^\cdot has been suggested for this oxidative addition reaction. Surprisingly, the reaction with Bu^\cdotI affords **15** only. Presumably, steric effects hinder attack of the *tert*-butyl radical at the metal center (130). However, in the presence of excess of reactive alkenes new products (**17**) were isolated in good yield [Eq. (21)]. A free radical chain reaction, initiated via a photochemical step, has been suggested for the formation of **17** (130).



Transfer of a methyl group has been observed in an oxidative addition reaction, when $[\text{PtMe}_2(\text{bipy})]$ is allowed to react with HgMeCl , PbMe_3Cl , or PbMe_4 [Eqs. (22) and (23)] (131). Reactions of halogens (X_2) with the



dinuclear platinum(II) complex $[\text{PtMe}_2(\mu\text{-dppm})_2\text{PtMe}_2]$ affords $[\text{PtMe}_3(\mu\text{-X})(\text{dppm})_2\text{PtMe}][\text{X}]$, while with methyl iodide the compound $[\text{PtMe}_3\text{-I}(\mu\text{-dppm})_2\text{PtMe}_2]$ is obtained (132). In the former reaction, transfer of a methyl group takes place to give a trimethylplatinum(IV) moiety. The reaction of $[\text{PtMe}_2(\mu\text{-dppm})_2\text{PtMe}_2]$ with 2 mol of iodine affords a mixture of the complexes $[\text{PtMe}_3(\mu\text{-I})(\mu\text{-dppm})_2\text{Pt(X)}][\text{I}_3]$ ($\text{X} = \text{Me}$ or I) (132).

Reactions of diiodo alkanes $\text{I}(\text{CH}_2)_n\text{I}$ ($n = 0-5$) with the platinum(II) compounds $[\text{PtMe}_2\text{L}_2]$ ($\text{L}_2 = \text{phen}$) afford $\{\text{PtMe}_2(\text{I})[(\text{CH}_2)_n\text{I}](\text{L}_2)_2\}$. The latter compounds react further with $[\text{PtMe}_2\text{L}_2]$ to give the dinuclear platinum(IV) complexes, $[\text{PtMe}_2(\text{I})\text{L}_2(\text{CH}_2)_n\text{PtMe}_2(\text{I})\text{L}_2]$ (133).

Trimethylplatinum(IV) complexes, with anionic bi- or tridentate ligands (134-142), such as Schiff bases, amino acids, and quinoline, have been

prepared by reaction of $[\text{PtMe}_3(\text{H}_2\text{O})_3]^+$ or $[\text{PtMe}_3\text{I}]_4$ with sodium or potassium salts of the ligand. Trimethylplatinum sulfate has also been used. The complexes with anionic bidentate ligands are generally dimeric. The donor atom, O, N, or S, forms a bridge between two platinum atoms (134,139,142). The bridge can be cleaved readily by tertiary phosphines or pyridine to give monomeric platinum(IV) complexes. Trimethyl-(theophyllinate)platinum(IV) is a trimeric complex with Pt—N-7 and Pt—N-9 bridges and a weak C-6—O—Pt bond (138). The complex reacts with excess of methylamine to give monomeric $[\text{PtMe}_3(\text{thp})(\text{MeNH}_2)_2]$. The bridges in dimeric amino acid complexes, $[\text{PtMe}_3(\text{AA})]_2$ (AA = L-alanine, L-valine), are weak and can be cleaved by methanol or water to give monomeric compounds (137).

C. Spectroscopic Properties

The Raman spectra of trimethylplatinum(IV) chloride, bromide, and iodide display strong lines at 581, 574, and 560 cm^{-1} , due to Pt—C stretching vibrations, but these are weak in the IR spectra (75). The Raman and IR spectra of $[\text{PtMe}_3(\text{OH})]_4$ and $[\text{PtMe}_3(\text{OD})]_4$ have also been reported (98,143–145). The IR bands at 147 and 126 cm^{-1} and Raman lines at 102 cm^{-1} have been attributed to the Pt_2O_4 skeletal deformation modes of $[\text{PtMe}_3(\text{OH})]_4$ (145). The single-crystal Raman polarization spectra of trimethylplatinum hydroxide, chloride, and iodide display strong low frequency Raman bands which have been assigned to platinum–platinum interactions in the tetramer, and these absorptions decrease with increasing intramolecular separations along the series X = OH, Cl, I (146). The absolute Raman intensities are taken to imply weak and highly ionic bonds between the platinum atoms and the bridging ligand X (146). Weak platinum–platinum interactions have also been observed in trimethylplatinum azide (76). Slightly acidic aqueous solutions of trimethylplatinum nitrate, sulfate, and perchlorate show a common line at 600 cm^{-1} in the Raman spectra, due to their dissociation to give the same aqua ion $[\text{PtMe}_3(\text{H}_2\text{O})_3]^+$ (78). The IR and Raman Pt—C stretching frequencies of some trimethylplatinum halides and pseudohalides are given in Table II.

For monomeric trimethylplatinum(IV) tertiary phosphine complexes, the Pt—C stretching frequencies generally appear in the region 540–615 cm^{-1} for methyl groups trans to halogen or phosphine ligands (10). The IR and Raman spectra of a series of complexes, $[\text{PtR}_2(\text{R}')(\text{X})\text{L}_2]$ (R = Me, CD_3 ; R' = Me, CD_3 , CF_3 , MeCO , PhCH_2 , $\text{CH}_2\text{—CH=CH}_2$; X = Cl, Br, I; L = PMe_2Ph , PMePh_2 , AsMe_2Ph , dppe), have been reported, and group trends have been correlated with changes in X or L (118). The Pt—C stretching bands observed

TABLE II
 $\nu(\text{Pt}-\text{C})$ AND ^1H -NMR DATA FOR SOME TRIMETHYLPLATINUM(IV) COMPOUNDS

Compound	$\nu(\text{Pt}-\text{C})^a$			^1H -NMR data			
	IR	Raman	Reference	Solvent	δ Pt—Me	$^2J(\text{Pt}-\text{H})$ in Hz	Reference
$[\text{PtMe}_3\text{Cl}]_4$	580 vw	581 vssh	75	C_6H_6	1.42	81.7	83
$[\text{PtMe}_3\text{Br}]_4$	573 vw	574 vssh	75	C_6H_6	1.54	80.1	83
$[\text{PtMe}_3\text{I}]_4$	559 vw	560 vs	75	C_6H_6	1.73	77.9	83
				C_6H_6	1.74	77.2	84
$[\text{PtMe}_3\text{OH}]_4$	570 vwsh	—	144	C_6H_6	0.95	80.1	83
	590 w			C_6H_6	0.86	78.5	84
$[\text{PtMe}_3\text{N}_3]_4$	560 w	581 vs	76	Acetone- d_6	-1.13	74.6	76
				C_6H_6	-0.98	74.1	76
$[\text{PtMe}_3\text{SMe}]_4$	—	566 vs	89	CDCl_3	0.97	69.7	89
$[\text{PtMe}_3(\text{H}_2\text{O})_3]^+$	—	600 vs	78	H_2O	1.08	79.7	100
$[\text{PtMe}_3\text{I}(\text{py})_2]$	—	—		PhNO_2	1.71	71.0	101
					1.30 ^b	69.1	
				CDCl_3	1.51	70.7	95
					1.21 ^b	69.5	
$[\text{PtMe}_3\text{I}(\text{bipy})]$	578 w	—	101	PhNO_2	1.81	70.8	101
	563 w				0.78 ^b	72.4	

^a vw = very weak, sh = shoulder, vs = very strong, w = weak.

^b Me group trans to I.

between 500 and 550 cm^{-1} are strong and clearly resolved in the Raman spectra but are weak in the IR spectra. Little change is observed in the positions of ν_{max} Pt—X for the series of complexes ν_{max} Pt—I in the range 128–132 cm^{-1} , ν_{max} Pt—Br in the range 153–169 cm^{-1} , and ν_{max} Pt—Cl in the range 243–255 cm^{-1} (118). The Pt—C stretching frequency for the methyl groups trans to L (L = nitrogen donor ligands) in $[\text{PtMe}_3(\text{X})\text{L}_2]$ remains relatively constant, while ν_{max} Pt—C for the methyl group trans to X varies (101). The following order of Pt—C stretching frequencies for the methyl group trans to X has been observed: NO , OAc , $\text{NCO} > \text{Cl} > \text{Br}$, $\text{NO}_2 > \text{I} \gg \text{CH}_3$.

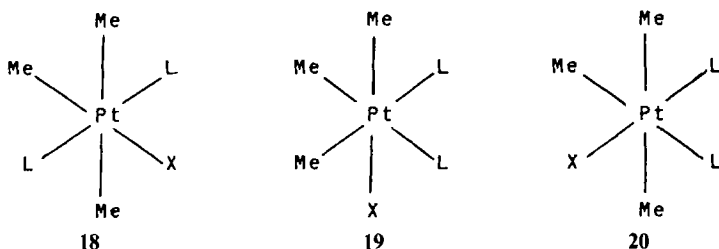
NMR spectroscopy has been widely used to determine the structures of triorganoplatinum(IV) complexes. The methyl complexes show well-resolved ^{195}Pt -methyl proton couplings in the ^1H -NMR spectra, and the magnitude of the coupling constant provides a useful diagnostic indication of the stereochemistry of the complex. Trimethylplatinum halides and pseudo-halides in general display single platinum-methyl resonances, with $^2J(\text{Pt}-\text{H})$ ranging from 75 to 82 Hz. Due to superposition, the ^1H -NMR spectrum of $[\text{PtEt}_3\text{Cl}]_4$ in CCl_4 was not analyzed (147). It was concluded that (1) the ^{195}Pt

nuclear spin orientation is identical for the interacting methylene and methyl resonances, and (2) $J(\text{Pt}-\text{Me})$ and $J(\text{Pt}-\text{CH}_2)$ have opposite sign (147).

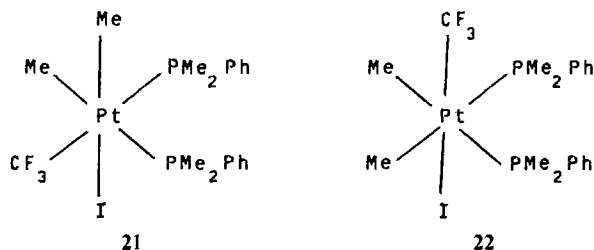
In aqueous solutions, trimethylplatinum nitrate, sulfate, perchlorate, acetate, formate, phosphate, and hydroxide give the trimethylplatinum aqua ion, $[\text{PtMe}_3(\text{H}_2\text{O})_3]^+$, as revealed by the $^2J(\text{Pt}-\text{H})$ value, which was the same (80.3 ± 0.3 Hz) for all seven complexes (83,142). The observation in the ^{17}O -NMR spectrum of perchlorate ion also indicate the formation of hydrated ion $[\text{PtMe}_3(\text{H}_2\text{O})_3]^+$ (148,149). The mean half-life time of water exchange (with free solvent water) was 1.4×10^3 seconds at 5°C (148). If excess ligand is present in water, the six-coordinated ions, $[\text{PtMe}_3\text{L}_3]^+$ ($\text{L} =$ ammonia, methylamine, pyridine) and $[\text{PtMe}_3\text{X}_3]^{2-}$ ($\text{X} =$ thiocyanate, nitrate, cyanide), are formed, and in which $^2J(\text{Pt}-\text{H})$ values are sensitive to the nature of groups (100). A stereochemically rigid tetrameric structure for trimethylplatinum thiocyanate has been suggested on the basis of ^1H -NMR data (79,81). The spectrum displays two sets of triplets in 2:1 ratio; one at low field (δ 1.48) has been assigned to the methyl groups trans to sulfur while the high-field signal (δ 1.06) is due to methyl groups trans to nitrogen.

The ^1H -NMR data indicate that the hydroxyl protons in tetrameric trimethylplatinum hydroxide are involved in hydrogen bonding (144). The presence of iodo and hydroxo bridging groups within the same tetrameric framework in $[\text{Pt}_4\text{Me}_{12}\text{I}_{4-n}(\text{OH})_n]$ has been established by ^1H -NMR spectroscopy (84,144). The $^2J(\text{Pt}-\text{OH})$ values vary from tetramer to tetramer, decreasing regularly from 11.2 Hz for $n = 4$ to < 2 Hz for $n = 1$ (84), indicating relatively less s character in the $\text{Pt}-\text{O}$ bonds of the mixed tetramers compared with that in $[\text{PtMe}_3(\text{OH})]_4$. Tetrameric structures have also been suggested for $[\text{PtMe}_3(\text{OMe})]_4$ (71), $[\text{PtMe}_3(\text{SH})]_4$ (150), and $[\text{PtMe}_3(\text{SR})]_4$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^i, \text{CH}_2\text{Ph}, \text{Ph}, \text{CF}_3$) (89,90,151). The ^1H -NMR spectrum of $[\text{PtMe}_3(\text{SMe})]_4$ displays a septet for SMe protons, due to coupling with zero, one, two, and three ^{195}Pt nuclei (89). The ^{13}C - and ^{195}Pt -NMR spectra of $[\text{PtMe}_3\text{X}]_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{OH}, \text{N}_3, \text{SMe}, \text{SPh}, \text{SCF}_3$) have been recorded, and long range coupling constants, e.g., $^{195}\text{Pt}-\text{Z}-\text{Pt}-^{13}\text{C}$, $^3J(\text{Pt}-\text{S}-\text{C}-\text{F})$, have been measured (151). The ^{195}Pt resonance frequency decreases in the order $\text{X} = \text{OH} > \text{SPh} > \text{SMe} > \text{N}_3, \text{Cl} > \text{Br}, \text{SCF}_3 > \text{I}$ (151). The complex $[\text{PtMe}_3(\text{OSiMe}_3)]$ is monomeric (152). The ^1H -NMR data for some of these compounds are given in Table II.

For monomeric trimethylplatinum(IV) complexes, formed with mono- or bidentate neutral donor ligands, three configurations have been proposed (18–20). Generally, configuration **19** predominates in solution, and in most cases only this isomer can be isolated. Complexes of the type $[\text{PtMe}_2(\text{R})(\text{X})\text{L}_2]$ ($\text{R} = \text{alkyl}, \text{acyl}$) also exist with structure **19** in which the R group is trans to X and the two methyl groups are trans to L . The $J(\text{Pt}-\text{Me})$ value is lower in these platinum(IV) complexes than that for the corresponding



platinum(II) complexes, and the value is very dependent on the nature of the trans ligand (10,11). For example, in tertiary phosphine or arsine complexes $J(^{195}\text{Pt}-\text{C}-^1\text{H})$ has values of 67–73 Hz (trans to halogen), 56–66 Hz (trans to L), and ~44 Hz (trans to carbon) (10). The complex $[\text{PtMe}_2(\text{CF}_3)\text{I}(\text{PMe}_2\text{Ph})_2]$ also exists with structure **19** in which the position of the trifluoromethyl group may be either trans to phosphine (**21**) or trans to the iodo group (**22**).



The ^1H -NMR resonance pattern of the *Pt*-Me groups for **22** is characteristic of two methyl groups trans to phosphine ligands and is similar to that found for complexes of the type *cis*- $[\text{PtMe}_2(\text{PR}_3)_2]$ (153), except that the central doublet is further split due to coupling with adjacent ^{19}F nuclei (153). The ^1H -NMR spectrum for isomer **21** was complex, due to inequivalence of the two *Pt*-Me and the four *P*-Me groups (154). The $^2J(\text{Pt}-\text{F})$ value was 425.8 ± 1.5 Hz while the $^3J(\text{P}-\text{F})$ values were $+10.9 \pm 0.6$ (cis) and $+60.4 \pm 0.8$ Hz (trans) (154).

Mono- and binuclear complexes of trimethylplatinum(IV), containing organochalcogen ligands, show a series of fluxional phenomena (102–117). For the binuclear complexes, $[(\text{PtMe}_3\text{X})_2(\text{MeSCH}_2\text{SMe})]$ ($\text{X} = \text{Cl}, \text{Br}$), activation energies for the sulfur inversion were estimated as 40.6 ± 0.3 and 48.9 ± 2.4 kJ/mol, respectively. These values are, respectively, 4 and 11 kJ/mol greater than the corresponding ring inversion energies (102). In

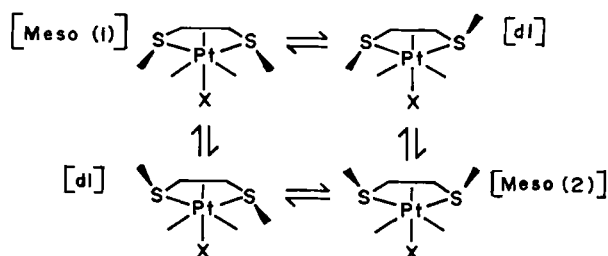


FIG. 3. Isomers of $[\text{PtMe}_3\text{X}(\text{MeSCH}_2\text{CH}_2\text{SMe})]$ formed by the independent inversion of either sulfur atom. [By permission from Elsevier Sequoia, S.A., E. W. Abel *et al.*, *J. Organomet. Chem.* **145**, C18 (1978) (102).]

mononuclear platinum complexes, the temperature-dependent changes in the *S*-Me proton signals have been explained on the basis of independent inversion at either sulfur atom (Fig. 3) (102).

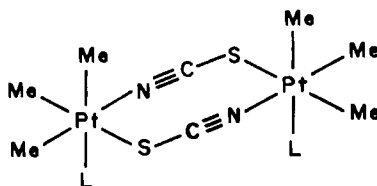
Ring reversal, pyramidal inversion at chalcogen atoms, and other fluxional rearrangements in the compounds $[(\text{PtMe}_3\text{X})_2(\text{MeECHREMe})]$ (*E* = S, Se) and $[(\text{PtMe}_3\text{X})_2(\text{MeSCH}_2\text{SeMe})]$ have also been investigated (106,108). In the binuclear complex $\{(\text{PtMe}_3\text{Br})_2[(\text{MeS})_2\text{C}=\text{C}(\text{SMe})_2]\}$ inversion at all sulfur atoms is fast at room temperature in CD_2Cl_2 , and on cooling to -70°C only two or three isomers predominate out of 16 possible isomers (113). The variable temperature NMR studies on mixed chalcogen ligand complexes of trimethylplatinum(IV), $[\text{PtMe}_3(\text{X})(\text{MeSRSeMe})]$ (*R* = CH_2CH_2 , *o*- C_6H_4), have shown that inversion at the S and Se atoms can be measured independently (111). At elevated temperatures, an intramolecular scrambling of all the *Pt*-Me sites occurs, associated with a fluxional movement which apparently results in a 180° rotation of the bidentate ligand (111). The energy associated with the process was of the order of 20 kJ/mol. The ^{13}C -, ^{77}Se -, and ^{195}Pt -NMR spectra of these complexes have also been recorded, and a considerable reduction in $^1J(\text{Pt}-\text{Se})$ values has been observed with expansion of the ligand ring (113).

The fluxional rearrangements in trimethylplatinum(IV) trithian complexes have been studied by dynamic NMR spectroscopy (107,109,114,116). The six-membered trithian ring in $[(\text{PtMe}_3\text{Cl})_2(\text{SCH}_2\text{SCH}_2\text{SCH}_2)]$ has a chair-boat conformation. The variable temperature NMR investigations demonstrated that the complexes undergo metal pivot and platinum-methyl intramolecular rearrangements (103,116). It was concluded that the former comprised a series of 90° 1,5-metal pivots and the latter was due to 120° rotations of methyl groups on the commuting Pt atom.

NMR spectroscopy has been used to study the trans influence of a series of ligands in the compounds $[\text{PtMe}_3(\text{X})\text{L}_2]$ (*L* = 1/2 bipy, 1/2 phen, 1/2 substituted 2,2'-bipyridine, or 1,10-phenanthroline, py, lut; X = uninegative

unidentate ligand) and $[\text{PtMe}_3(\text{bipy})\text{L}'][\text{ClO}_4]$ (L' = monodentate neutral ligand) (94). The magnitude of $^2J(\text{Pt}-\text{H})$ for the methyl group was markedly dependent on the nature of the ligands trans to it. Smaller variations have been observed in $^2J(\text{Pt}-\text{H})$ for the methyl groups trans to L as X varied (< 6 Hz), and for the methyl group trans to I as the ligand L varied (< 5 Hz). The following order of the trans influence has been found for a series of ligands (94): $\text{Me} > \text{CN} > \text{PPh}_3 > \text{NO}_2 > \text{amines, py, SCN} > \text{NCO, NCS, I} > \text{Br, Cl} > \text{OAc} > \text{NO}_3 > \text{H}_2\text{O}$.

The dimeric platinum complexes $[\text{PtMe}_3(\text{SCN})\text{L}]_2$, prepared from $[\text{PtMe}_3(\text{SCN})]_4$ and L ($\text{L} = \text{py, PPh}_3, \text{AsPh}_3$), display three lines for the Pt-Me protons in their $^1\text{H-NMR}$ spectra. Structure 23 has been suggested (81).



23

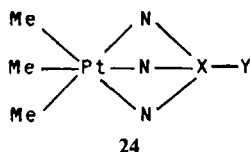
Variable temperature $^1\text{H-NMR}$ spectroscopy has shown that the xanthate complexes $[\text{PtMe}_3(\text{S}_2\text{COR})]_2$ ($\text{R} = \text{Me, Et, Pr}^i, \text{Bz}$) are stereochemically nonrigid above -40°C in CDCl_3 solution, while the dithiocarbamate complexes $[\text{PtMe}_3(\text{S}_2\text{CNR}_2)]_2$ are stereochemically rigid at room temperature (135).

The Schiff base (SalNR) and oxinate complexes are dimeric in the solid state as well as in solution, and contain oxygen bridges between the two platinum atoms (83,139,140,142). The bridged Pt—O bonds in the oxinate complex $[\text{PtMe}_3(\text{Ox})]_2$ appear to be nonequivalent, since three methyl resonances appear in the $^1\text{H-NMR}$ spectrum with three different $^2J(\text{Pt}-\text{H})$ values (70.3, 76.0, and 80.4 Hz) (83). The monomeric complexes formed by bridge-cleavage reactions with monodentate ligands show three nonequivalent Pt-Me signals as triplets.

The variable temperature $^1\text{H-NMR}$ spectra of the amino acid complexes $[\text{PtMe}_3(\text{AA})(\text{CD}_3\text{OD})]$ and $\text{Na}[\text{PtMe}_3(\text{AA})_2]$ ($\text{AA} = \text{L-alanine, L-valine}$) have shown that rapid intramolecular exchange reactions take place in solution (136,137). When the α -carbon atom of the amino acid is an asymmetric center, a mixture of diastereoisomers is formed, and all of them are observed in the $^1\text{H-NMR}$ spectra (137).

The $^1\text{H-NMR}$ spectra of $[\text{PtMe}_3(\text{pz}_4\text{B})]$, $[\text{PtMe}_3(\text{pz}_3\text{BH})]$, and the cationic complexes $[\text{PtMe}_3(\text{pz}_3\text{CH})]^+$ and $[\text{PtMe}_3(\text{py}_3\text{CH})]^+$, display only a single methyl platinum resonance with platinum satellites (96,155). Structure

24 has been proposed for these species. Similarly, the ^{13}C -NMR spectra of the cationic complexes display a single *Pt*-Me resonance with a $^1J(\text{Pt}-\text{C})$ value of 688 ± 1 Hz (96). The complex derived from bis(1-pyrazolyl)borate shows a strong broad infrared band at 2039 cm^{-1} , attributed to intramolecular *Pt*-H bonding (155).



(X = B or C;

Y = H or pz;

N = py or pz)

The tetrameric structures of trimethylplatinum azide and the mercapto complexes have been established by their mass spectra, which display molecular ion peaks for tetramers (76,90). The second most intense peak in the spectrum of $[\text{PtMe}_3\text{N}_3]_4$, at m/e 240 is due to the $[\text{Me}_3\text{Pt}]^+$ fragment which reveals great stability for this cation (76). The extreme sturdiness of this group in the aqua ion has been shown by its polarogram which shows four well-separated waves at high negative potentials (-1.05 , -1.035 , -1.55 , and -1.8 V) (156).

The crystal structures of some triorganoplatinum(IV) complexes have been determined (86–88,132,157–163). In all cases platinum adopts the highest coordination six, either by oligomerization or complexation with various ligands. The X-ray crystallographic data for triorganoplatinum(IV) compounds are summarized in Table I.

The X-ray structural analyses of various trialkylplatinum halides and pseudohalides, $[\text{PtMe}_3\text{Cl}]_4$ (86,164), $[\text{PtMe}_3\text{I}]_4$ (73,162,165), $[\text{PtMe}_3\text{N}_3]_4$ (166), $[\text{PtMe}_3(\text{OH})]_4$ (87,88,161), and $[\text{PtEt}_3\text{Cl}]_4$ (163), have shown that they are tetrameric, with platinum and X (X = Cl, I, N_3 , OH) at alternate corners of a cube. The α -nitrogen atom of the azido groups in trimethylplatinum azide links three platinum atoms of a tetrameric cubane moiety (166). The hydroxyl oxygen of the $[\text{PtMe}_3(\text{OH})]_4$ participates in bridge formation (87,88,161) (Fig. 4). Some important bond lengths and angles for the species $[\text{PtR}_3\text{X}]_4$ are given in Table III.

An X-ray analysis of $[\text{PtMe}_2(\text{OOPr}^i)(\text{I})(\text{phen})]$ has confirmed the presence of a peroxyalkyl-platinum linkage in the complex (129). The platinum atom has an octahedral coordination (Fig. 5) with a *Pt*-O bond length of $2.032(6)$ Å and *Pt*-O-O angle $110.2(4)^\circ$.

The chelate ring in $[\text{PtMe}_3(\text{I})(\text{PhMeAsCH}_2\text{CH}_2\text{AsMePh})]$ has a distorted envelope conformation (157). The crystals of $\{\text{PtMe}_3(\text{I})[(\text{Me}_2\text{pz})_2\text{CH}_2]\}$ are

TABLE III
IMPORTANT BOND LENGTHS AND ANGLES IN SOME TRIALKYLPLATINUM(IV) HALIDES AND PSEUDOHALIDES

Compound	Pt—Pt (Å)	Pt—X (Å)	Pt—C (Å)	X—Pt—X (°)	Pt—X—Pt (°)	Reference
[PtMe ₃ Cl] ₄	3.73(0.03)	2.48(0.11)	—	81	99	86
[PtMe ₃ I] ₄	—	2.83	—	93.2	90.0, 86.4	165
[PtMe ₃ OH] ₄	3.41(0.04)	2.20(0.04)	2.02(0.03)	78(2)	102(2)	161
	3.430(0.002)	2.22(0.01)	2.04(0.02)	77.6(0.2)	101.2(0.2)	88
[PtMe ₃ N ₃] ₄	3.449(0.004)	2.255(0.05)	2.047(0.06)	79.5	100.1	166
[PtEt ₃ Cl] ₄	3.903(0.015)	2.58(0.05)	2.07(0.11)	81(2)	98	163

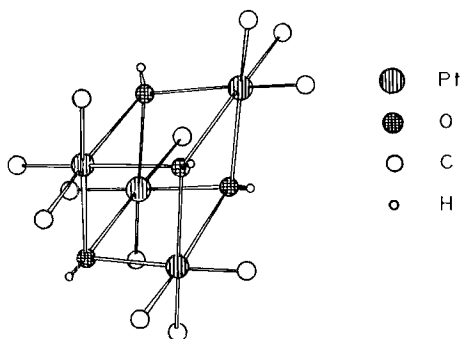


FIG. 4. Molecular structure of [PtMe₃OH]₄. [By permission from Elsevier Sequoia, S.A., H. S. Preston, J. C. Mills, and C. H. L. Kennard, *J. Organomet. Chem.* **14**, 447 (1968) (161).]

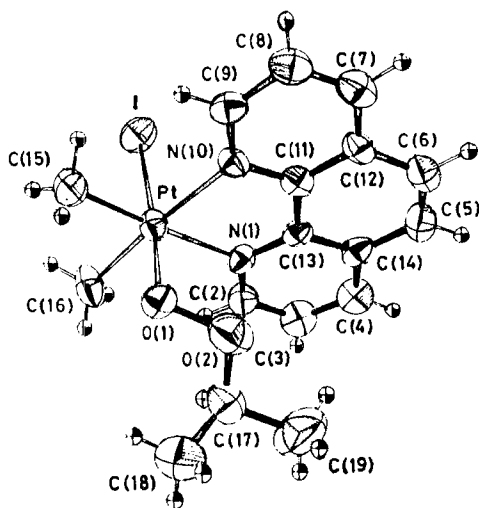
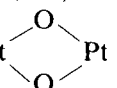


FIG. 5. X-Ray structure of [PtMe₂(OOPrⁱ)I(phen)]. [By permission from the Royal Society of Chemistry, G. Ferguson *et al.*, *J. Chem. Soc., Chem. Commun.*, 267 (1983) (129).]

orthorhombic, space group *Pcmn* (96). The Pt—I distance [2.843(1) Å] is one of the longest Pt—I bond distances yet reported for organoplatinum(IV) compounds, illustrating the strong trans influence of the methyl group (96). The six-membered PtN₄C ring has a boat conformation, with a Pt—C-6 fold angle of 119.7° (Fig. 6).

Trimethylplatinum oxinato (159,160) and salicylaldehydato (158,159) complexes are dimeric, involving Pt  Pt bridges with a Pt—O distance

of 2.24 ± 0.03 Å. Each platinum atom is six coordinated with *cis*-methyl groups. The strain in the formation of a four-membered ring is shared by the platinum and oxygen atoms; all have bond angles 10° less than the ideal value. The structure of the oxinate complex is shown in Fig. 7.

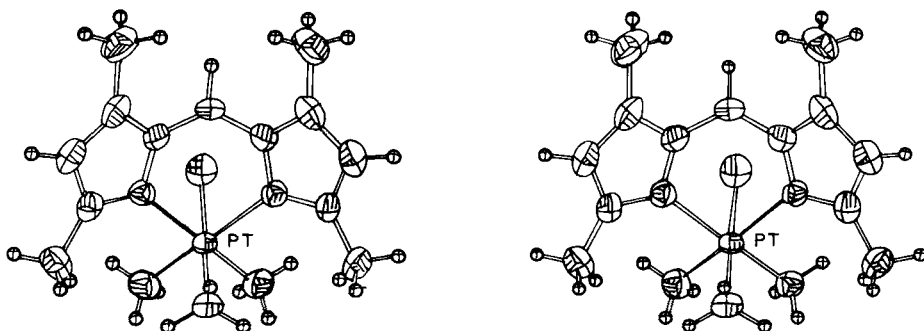


FIG. 6. Stereoview of {PtMe₃(I)}[(Me₂pz)₂CH₂] molecule. [By permission from Elsevier Sequoia, S.A., H. C. Clark, G. Ferguson, V. K. Jain, and M. Parvez, *J. Organomet. Chem.* **270**, 365 (1984) (96).]

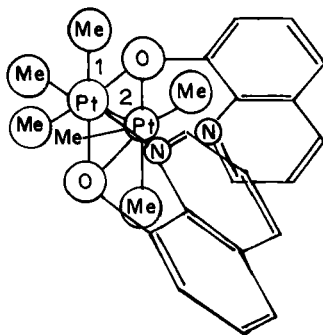


FIG. 7. Molecular structure of [PtMe₃Ox]₂. [By permission from the Royal Society of Chemistry, J. E. Lydon and M. R. Truter, *J. Chem. Soc. A*, 6899 (1965) (160).]

The X-ray structural analysis of $[\text{Pt}_2\text{Me}_4(\text{Br})_2(\mu\text{-CH}_2\text{C}_6\text{H}_4\text{CH}_2)(\text{dppm})]$, obtained by reaction of $[\text{Pt}_2\text{Me}_4(\text{Br})_2(\mu\text{-CH}_2\text{C}_6\text{H}_4\text{CH}_2)(\text{AsMe}_2\text{Ph})_2]$ (from *cis*- $[\text{PtMe}_2(\text{AsMe}_2\text{Ph})_2]$ and *o*-xylylene dibromide) with dppm in benzene, has shown that each platinum has an approximately octahedral environment. The two platinum atoms are bridged by the *o*-xylene and dppm ligands, which are trans to each other, and form a nine-membered ring in the chair conformation (Fig. 8) (167).

The crystal and molecular structures of some dinuclear trimethylplatinum-(IV) complexes containing sulfur or selenium ligands have been determined (103,107,110,115,116). The platinum atoms in all of them possess an octahedral environment. The two platinum atoms are held together by three bridging groups; two of them are conventional halogen bridges, and the third is bisulfur or biselenium bridge. In $[(\text{PtMe}_3\text{Br})_2(\text{MeSe-SeMe})]$, the Se—Se bond length is 1.19 Å shorter than the Pt—Pt contact distance. Thus, it is not possible for the four atoms of the Pt_2Br_2 ring to be coplanar, although the platinum atoms retain an approximately octahedral environment. Therefore, in the Pt_2Br_2 moiety an angle of 29° between the normals of the planes of the two Br—Pt—Br fragments has been observed (Fig. 9) (103).

The trithiane platinum complex $[(\text{PtMe}_3\text{Cl})_2(\text{SCH}_2\text{SCH}_2\text{SCH}_2)]$ also contains three bridges; two of them are chlorine, and the third is the S_3C_3 ring. To span the two platinum atoms, distortion in the S_3C_3 ring, via stretching of the S-1—S-2 distance, has been observed (Fig. 10) (107). The ring itself has an unusual distorted boat conformation.

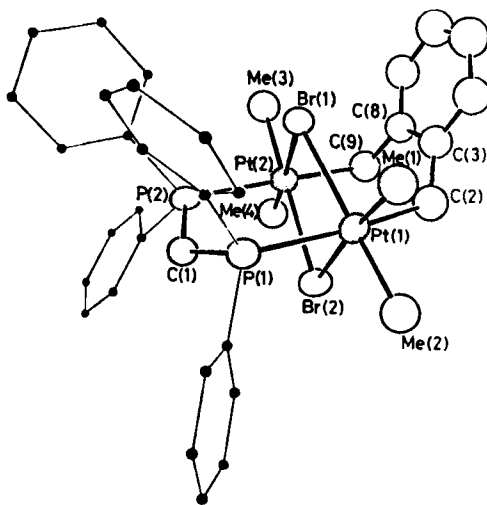


FIG. 8. X-Ray structure of $[\text{Pt}_2\text{Me}_4(\text{Br})_2(\mu\text{-CH}_2\text{C}_6\text{H}_4\text{CH}_2)(\mu\text{-dppm})]$. [By permission from the Royal Society of Chemistry, A. T. Hutton, B. Shabanzadeh, and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1345 (1982) (167).]

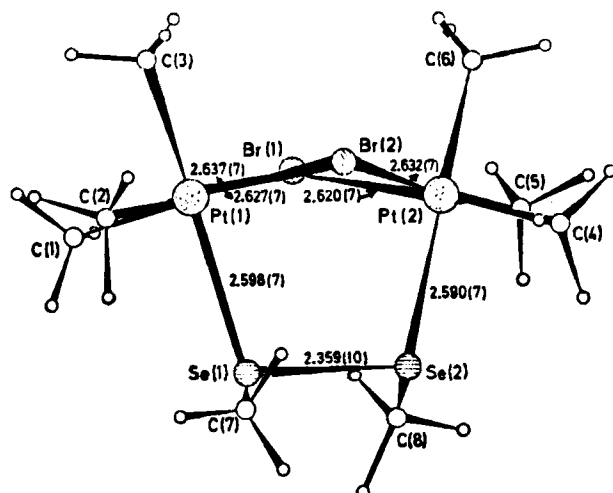


FIG. 9. X-Ray structure of $[(\text{PtMe}_3\text{Br})_2(\text{MeSeSeMe})]$. [By permission from the Royal Society of Chemistry, E. W. Abel *et al.*, *J. Chem. Soc., Chem. Commun.*, 713 (1979) (103).]

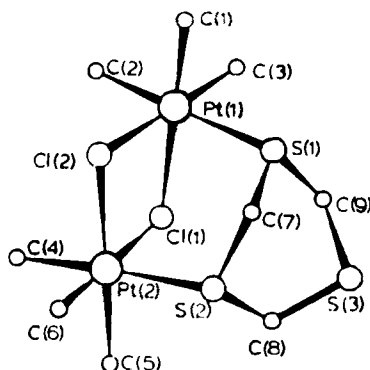


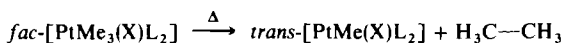
FIG. 10. Molecular structure of $[(\text{PtMe}_3\text{Cl})_2(\text{SCH}_2\text{SCH}_2\text{SCH}_2)]$. [By permission from the Royal Society of Chemistry, E. W. Abel *et al.*, *J. Chem. Soc., Chem. Commun.*, 29 (1981) (107).]

D. Chemical Properties

Triorganoplatinum(IV) compounds undergo reductive elimination reactions to give alkanes and organoplatinum(II) complexes. The relative ease of alkane elimination depends upon the alkyl group, and the following order has been observed: $\text{MeCO} > \text{CH}_2\text{CH}=\text{CH}_2$, $\text{Et} > \text{Me} > \text{CD}_3 > \text{PhCH}_2 > \text{Ph} > \text{CF}_3$. Trimethylplatinum(IV) complexes containing tertiary phosphines or arsines when heated above their melting points under reduced pressure

give exclusively ethane (34). However, in case of $[\text{PtMe}_3\text{Cl}(\text{PMe}_2\text{Ph})_2]$ small amounts of methyl chloride along with ethane are also formed (34). Pyrolysis of $[\text{PtMe}(\text{Ph})_2(\text{I})(\text{PMe}_2\text{Ph})_2]$ or $[\text{PtMe}_2(\text{Bz})(\text{X})(\text{PMe}_2\text{Ph})_2]$ yields toluene or ethylbenzene, respectively (121,168). The acetyl compounds $[\text{PtR}_2(\text{Ac})(\text{X})\text{L}_2]$ ($\text{R} = \text{CH}_3, \text{CD}_3$) give acetone and *trans*- $[\text{PtR}(\text{X})\text{L}_2]$ (34,121,168).

Owing to the much greater strength of the $\text{Pt}-\text{CF}_3$ bond, compared with the $\text{Pt}-\text{Me}$ bond, pyrolysis of $[\text{PtMe}_2(\text{CF}_3)(\text{I})(\text{PMe}_2\text{Ph})_2]$ eliminates both methyl groups as ethane (122). A kinetic study of the reaction



$\text{L} = \text{monodentate tertiary phosphine}$

indicates that the first stage involves loss of a phosphine ligand followed by intramolecular reductive elimination of ethane from the five-coordinate trimethylplatinum(IV) intermediate (125). The loss of phosphine reduces the electron density at the five-coordinate intermediate, and facilitates reductive elimination. The complexes $[\text{PtMe}_3(\text{X})(\text{dppe})]$ also eliminate ethane without prior dissociation of phosphine ligand. In this case the activation energy (69 kJ/mol) for ethane elimination is lower than the methylplatinum bond energy (144 kJ/mol).

On pyrolysis, $[\text{PtMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)(\text{X})(\text{PMe}_2\text{Ph})_2]$ loses the allyl group preferentially, and a mixture of gases (methane, ethane, propene, but-1-ene, and hexa-1,5-diene) is formed. The formation of products other than ethane and but-1-ene has been explained by a free radical mechanism, while ethane and but-1-ene are formed by an intramolecular concerted mechanism (168). Deuterium labeling studies have shown that an intramolecular concerted mechanism is responsible for reductive elimination of ethane from $[\text{PtR}_2(\text{R}')(\text{I})(\text{PMe}_2\text{Ph})_2]$ ($\text{R} = \text{Me}, \text{CD}_3$; $\text{R}' = \text{Me}, \text{CD}_3$) (169). The CH_3 groups are eliminated more easily than CD_3 groups. It has been observed that the groups trans to phosphine leave preferentially (170).

Trimethylplatinum(IV) compounds containing nitrogen donor ligands appear to be stable with respect to reductive elimination. The complex $[\text{PtMe}_3(\text{I})(\text{py}_2\text{CH}_2)]$ is stable at about 200°C and decomposes at around 240°C without elimination of ethane or methyl iodide (96). Compounds of the form $[\text{Pt}(\text{Me})\text{Ph}_2(\text{I})\text{L}_2]$ ($\text{L}_2 = \text{bipy}, \text{phen}$) are stable below 200°C (126), while similar compounds containing dimethylphenylphosphine cannot be isolated due to reductive elimination reactions at ambient conditions (121). The complex $[\text{PtMe}_3(\text{X})(\text{py})_2]$ on heating loses pyridine in two steps to give $[\text{PtMe}_3\text{X}]_4$ rather than undergoing a reductive elimination reaction (97). For reductive elimination to occur, the following general conditions must be met: (1) two of the three methyl groups must be trans to ligands of high trans

influence; and (2) the three methyl groups must not be chemically equivalent. For example, *fac*-[PtMe₃L₃]⁺ (L = H₂O, MeOH, py, PMe₂Ph, etc.) complexes are quite stable with respect to reductive elimination while *fac*-[PtMe₃(PMe₂Ph)(L)]⁺ (L = Low trans influence ligand such as MeOH, Me₂CO, SbPh₃, AsPh₃) reduces rapidly to platinum(II).

The UV photolysis of [Pt(Me)Ph₂(I)(bipy)], [PtMe₃(I)(bipy)], and [Pt(CD₃)₃(I)(bipy)] gives a number of products, formation of which involve free radicals in the primary photolytic steps (70). The compounds [PtMe₃X] (X = Cl, Br, I) have been used for preparing highly dispersed supported platinum catalysts such as Pt/SiO₂ and Pt/Al₂O₃ (171–173). They have also been used in hydrosilylation and polymerization reactions, especially for the preparation of polysiloxanes (174–178).

V

TETRAORGANOPLATINUM(IV) COMPOUNDS

Although a number of claims have been made for the synthesis of tetramethylplatinum(IV) (7,85,179), all of them were later shown to be in error (87,88,180). The product isolated by earlier workers was trimethylplatinum hydroxide, the hydroxyl group having been shown to possess the same diffraction properties as is anticipated for Me in tetramethylplatinum(IV) (87,88,161). In a patent the synthesis of [Pt(CF₃)₄] has been claimed (181).

Tetramethylplatinum(IV) complexes containing stabilizing ligands have, however, been successfully prepared either by the reaction of [PtMe₃(I)L₂] (L = PMe₂Ph, AsMe₂Ph, bipy) with excess methyllithium (51,101) or by the reaction of dinuclear [PtMe₄(μ-SMe₂)]₂ with L' (2 L' = dppm, dppe, bipy, phen; L' = PMe₂Ph, PMePh₂) (182). In all of these complexes donor ligands occupy the *cis* positions. The infrared spectrum of [PtMe₄(bipy)] displays a very intense band at 480 cm⁻¹ due to the Pt—C absorption. In chloroform it decomposes to [PtMe₃(Cl)(bipy)]. The phosphine or arsine complexes on heating at 160°C gave ethane and *cis*-[PtMe₂(ER₃)₂] (E = P, As) (51).

Although the compound tetramethylplatinum(IV) has not been reported, penta- and hexamethylplatinate ions are known (182a,182b). Treatment of [PtMe₃I]₄ with excess methyllithium in Et₂O yields Li₂[PtMe₆]. The hexamethylplatinate(IV) species can also be obtained in solution by the reaction of MeLi/LiI with [NBu₄]₂[PtCl₆] in diethyl ether at -78°C. If MeLi/LiBr is used in this synthesis, the complex [NBu₄]₂[PtMe₆] is precipitated, along with lithium halides (182b). Solid [Bu₄N][PtMe₆] is stable under nitrogen at room temperature, but diethyl ether solutions of [PtMe₆]²⁻ decompose in the absence of MeLi.

When $[\text{PtMe}_3\text{I}]_4$ is treated with MeLi in the presence of 1 equivalent of PPh_3 , or when $[\text{PtMe}_4(\text{PMe}_2\text{Ph})_2]$ is treated with halide-free MeLi, the pentamethylplatinate ion is formed, which on prolonged standing gives $\text{Li}_2[\text{PtMe}_6]$ (182a). The ^1H -NMR spectrum of the hexamethylplatinate ion displays a single methyl resonance at δ 0.55, with a $^2J(\text{Pt}-\text{H})$ value of 40.0 Hz. The low value of the coupling constant is indicative of the presence of mutually trans methyl groups (182a). The Raman spectrum of this ion is consistent with the presence of an essentially octahedral environment around the platinum atom.

Triorgano(cyclopentadienyl)platinum(IV) complexes and triorganoplatinum(IV) β -diketonates are well-known examples of the PtC_4 unit. Cyclopentadienyl derivatives have been prepared by the reaction of $[\text{PtR}_3\text{I}]_4$ with sodium or thallium cyclopentadienide (152,183–185). The complex $[\text{PtMe}_3\text{Cp}]$ is volatile and can be sublimed under reduced pressure at 20°C and 10^{-2} mm Hg (152). The compounds $[\text{PtR}_3\text{Cp}]$ are monomeric in nature and have no tendency to form adducts with donor ligands. In the Raman spectrum of $[\text{PtMe}_3\text{Cp}]$ polarized lines at 561 and 263 cm^{-1} have been assigned to symmetric $\text{Pt}-\text{Me}$ and $\text{Pt}-\text{Cp}$ stretching vibrations (186). The ^1H -NMR spectrum displays single resonance for the Cp protons at δ 5.61, with a $^2J(\text{Pt}-\text{H})$ value of 5.8 Hz (152,183). The IR, ^1H - and ^{13}C -NMR spectra (152,183,185,188) and the mass (184,189) spectral data reveal pentahepto bonding of the C_5H_5 ligand to the platinum atom. However, Fritz and Schwarzhans (187) have proposed a diene-type structure for the ring. The sandwich structure suggested on the basis of spectroscopic studies has been confirmed by X-ray analysis of $[\text{PtMe}_3\text{Cp}]$ (190,191). The cyclopentadienyl ring is symmetrically bound to platinum which lies above a point approximately at the center of the five-membered ring (Fig. 11). No disorder is observed in the positions of the carbon atoms. The C_5H_5 ring lies parallel to the plane of the three methyl groups.

The complexes $[\text{PtRR}'\text{R}''\text{Cp}]$ ($\text{R} = \text{R}' = \text{Me}$, $\text{R}'' = \text{Me}$, Ac, Et; $\text{R} = \text{R}' = \text{Et}$, $\text{R}'' = \text{Me}$, Ac; $\text{R} = \text{Me}$, $\text{R}' = \text{Et}$, $\text{R}'' = \text{Ac}$) have been studied by ^1H - and

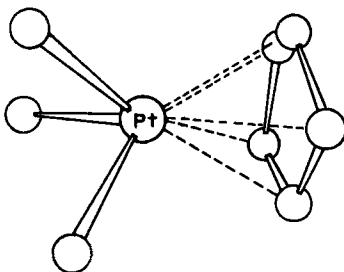


FIG. 11. Molecular structure of $[\text{PtMe}_3\text{Cp}]$. [By permission from the Royal Society of Chemistry, J. J. Daly, G. W. Adamson, and J. C. J. Bart, *J. Chem. Soc. A*, 2616 (1971) (191).]

^{13}C -NMR spectroscopy (185,188). The molecule $[\text{PtMe}(\text{Et})(\text{Ac})\text{Cp}]$ is chiral in nature (185). The methyl groups in $[\text{PtMe}_2(\text{Ac})\text{Cp}]$ become diastereotopic in the presence of the chiral shift reagents (188). The relative steric hindrance between the ring and the substituents on the platinum atom has been studied by mechanical spectroscopy (192).

Gaseous $[\text{PtMe}_3\text{Cp}]$ decomposes homogeneously into platinum and methane at 165°C with a half-life of $\sim 10^3$ seconds. The primary reaction step involves separation of a methyl radical (193). The bond dissociation energy has been estimated at 39 ± 5 kcal/mol. Irradiation of $[\text{PtMe}_3\text{Cp}]$ led to clean homolysis of a $\text{Pt}-\text{Me}$ bond with no competing cyclopentadienyl dissociation (194).

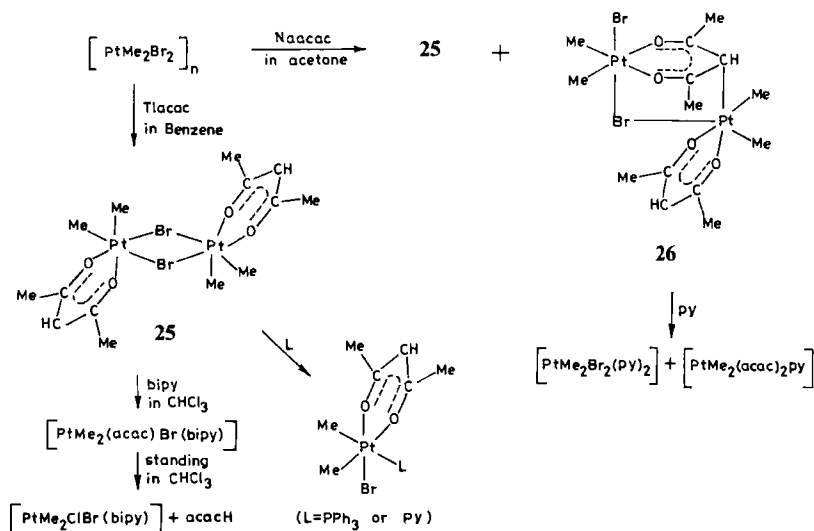
VI

ORGANOPLATINUM(IV) β -DIKETONATES AND RELATED COMPOUNDS

Organoplatinum(IV) β -diketonates have been prepared by treating organoplatinum halides with thallium or potassium salts of the β -diketone (93,195–199). They may also be obtained by the reaction between $[(\text{PtMe}_3)_2\text{SO}_4]$ and sodium salt of the β -diketone (200). A similar reaction with nickel salts of thio- β -diketone or β -ketoimine gave the corresponding trimethylplatinum thio- β -diketonates or β -ketoiminates. Treatment of the salts of $[\text{PtMe}_2(\text{Br})(\text{H}_2\text{O})_3]^+$ with acacH (38,41) produced species of composition $[\text{PtMe}_2(\text{Br})(\text{acac})_2]$ and $[\text{PtMe}_2(\text{Br})_2 \cdot \text{PtMe}_2(\text{acac})_2]$. Some of the reactions of dimethylplatinum(IV) β -diketonates are shown in Scheme 2.

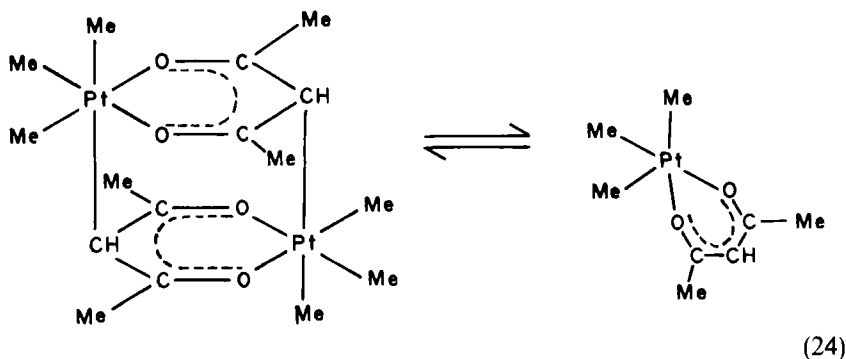
Dimethylplatinum(IV) β -diketonates are dimeric, and their structure is dependent on the method of preparation. Thus reaction of $[\text{PtMe}_2\text{Br}_2]_n$ with $\text{Tl}(\text{acac})$ gives a compound with configuration **25**, in which the bromine atoms participate in dimerization. A similar reaction with $\text{Na}(\text{acac})$, however, gives a mixture of two compounds (**25** and **26**) (38). Compound **26** has also been shown to be dimeric, with two bromine atoms associated with one platinum and the two acac ligands with the other metal center. Both **25** and **26** react with L ($\text{L} = \text{PPh}_3$, py) to give mononuclear complexes (38).

Trimethylplatinum(IV) β -diketonates, thio- β -diketonates, and β -ketoiminates, represented here as $[\text{PtMe}_3(\text{Chel})]$, are dimeric both in solution and in the solid state. The ligands behave as tridentate groups (83,200–202). Dimerization of β -diketone and β -ketoimine complexes takes place through the γ -carbon atom, as demonstrated by ^1H -NMR spectroscopy (83,101,200,202–204). The variable temperature ^1H -NMR spectra for the complexes $[\text{PtMe}_3(\text{Chel})]_2$ [$\text{Chel} = \text{malondialdehyde}$, acetoacetaldehyde , acac , dibm , acacR ($\text{R} = \text{NH}$, NMe)] revealed evidence for a rapid dissociation involving cleavage of the platinum- γ -carbon bond (202) rather than the



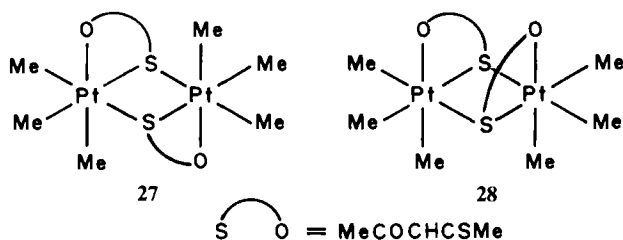
SCHEME 2

cleavage of Pt—O bonds (83). The dissociation led to five-coordinate trimethylplatinum(IV) species [Eq. (24)]. The activation energy for this process is 61.5 ± 0.8 kJ/mol (205). Trimethylplatinum(IV) β -ketoester complexes, however, are kinetically rigid at room temperature and do not show this exchange phenomena (206).



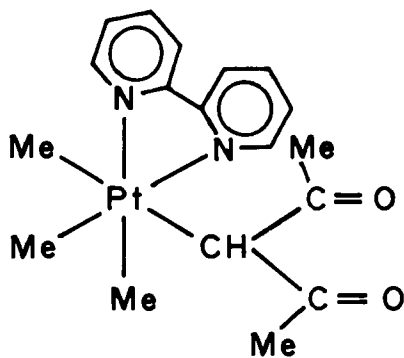
The γ -carbon atom in thio- β -diketone complexes does not participate in bonding with the platinum atom. Dimerization in these complexes takes place via sulfur atoms, and the bonds appear to be highly unsymmetrical (200). The complex $[\text{PtMe}_3(\text{Sacac})]_2$ (Sacac = MeCOCHCSMe) exists as a mixture of two isomers in solution (27 and 28).

The dimeric structure of β -diketone complexes has been confirmed by X-ray structural analysis (196,207–210). The location of hydrogen atoms in

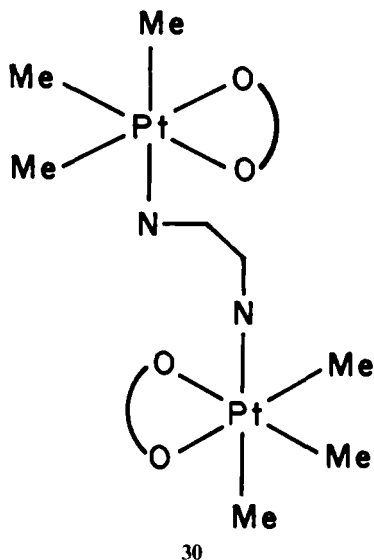


trimethyl(nonane-4,6-dionato)platinum(IV) has been determined by neutron diffraction methods (211). The Pt—C γ —H angle is 98(4)°. Thermal decomposition of [PtMe₃(acac)]₂ at 250–450°C gives a mixture of gaseous products and platinum metal (212). Hence the complex has been used to obtain low carbon-content platinum coatings (213,214).

The bridge in dimeric [PtMe₃(Chel)]₂ can be cleaved by mono- or bidentate neutral donor ligands to give mononuclear complexes, the structure of which is determined by the nature of the chelating and L ligands (197,200–215). Thus the complexes [PtMe₃(β -dik)]₂ (β -dik = acac, dibm) react with L (= py, quinoline, aniline, NH₃, lut, Me₂S, PPh₃) to give monomeric [PtMe₃(β -dik)L] in which the β -diketone ligand is bonded to platinum through both oxygen atoms. Similarly, cleavage of thio- β -diketone complexes with L gives monomeric complexes containing the chelated thio- β -diketone ligand (200). Cleavage with bidentate ligands such as bipy or phen also affords mononuclear compounds, but the Chel ligand acts as an unidentate moiety. The β -diketone complexes show bonding through the γ -carbon atom (29) (197,200,216,217), as confirmed by X-ray diffraction studies of [PtMe₃(acac)(bipy)] (217). The thio- β -diketone complexes, however, bond through the sulfur atom (200).



Reaction of ethylenediamine or *meso*-1,2-diphenyl-1,2-diamino ethane with $[\text{PtMe}_3(\text{acac})]_2$ affords another dinuclear complex $\{[\text{PtMe}_3(\text{acac})]_2(\text{en})\}$, which contains a chelating acac ligand (197,218). A crystal structure determination (218) for $[\{[\text{PtMe}_3(\text{acac})]_2(\text{en})\}]$ established the structure **30**.



The complexes $[\text{PtMe}_3(\text{acac})(\text{L})]$ (L = a monodentate ligand) show in their $^1\text{H-NMR}$ spectra small couplings (~ 2 Hz) between platinum and the γ -proton of the acac ligand (200). At higher temperatures exchange phenomena have been observed. The $\text{Pt}-\gamma\text{-CH}$ bond in $[\text{PtMe}_3(\text{acac})(\text{L})]$ (L = bipy, phen) may be stronger than in $[\text{PtMe}_3(\text{acac})]_2$ indicated from the magnitude of $J(\text{Pt}-\gamma\text{-CH})$ in the former (101,219,220). The relative signs of $^2J(\text{Pt}-\text{H})$ and $^1J(\text{P}-\text{H})$ for $[\text{PtMe}_3(\text{acac})(\text{PPh}_3)]$ have been shown to be opposite for both *cis*- and *trans*-methyl groups. Each $^2J(\text{Pt}-\text{H})$ is negative and $^3J(\text{P}-\text{H})$ is positive for the *cis* coupling and negative for *trans* coupling (205).

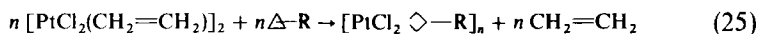
VII

PLATINACYCLOALKANES

In spite of their discovery over 30 years ago, interest in metallacycloalkane chemistry has increased during recent years as a result of their implication in several transition metal-catalyzed reactions. Following the suggestion of

Walsh (221) that there is considerable delocalization of electrons in the cyclopropane ring. Tipper (222) examined the ability of cyclopropane to form metal complexes analogous to those of olefins or acetylenes. Thus he treated chloroplatinic acid with cyclopropane in acetic anhydride and obtained a compound of composition $[\text{PtCl}_2(\text{C}_3\text{H}_6)]_n$. It was suggested that the cyclopropane moiety in the complex behaves as an unsaturated ligand like ethylene. Subsequent research has shown that the complex is a chloride-bridged tetramer with a structure analogous to platinum(IV) alkyls in which platinum has inserted into the cyclopropane ring (223,224).

Tipper's original synthesis of platinacyclobutanes could not be extended to the preparation of substituted derivatives since pyrylium ion salts are formed rather than platinacyclobutanes. A more general method for synthesizing substituted platinacyclobutane complexes has been discovered by McQuillin *et al.* (225–227). This method involves reaction of Zeise's dimer $([\text{Pt}(\mu\text{-Cl})\text{Cl}(\eta\text{-C}_2\text{H}_4)]_2)$ with the desired substituted cyclopropane in diethyl ether or THF [Eq. (25)]. An electrophilic attack by Pt(II) on the organic ring

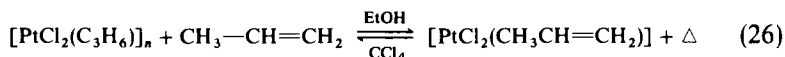


has been proposed (227). The displacement of ethylene from the Zeise's dimer depends on the electron donor capacity of the cyclopropane ring. Thus reactions are inhibited by electron-withdrawing substituents. The reactivity of the substituted cyclopropane falls in the following order of substituent R: alkyl > aryl \gg CO_2Me , COMe , CN . Complex formation is not observed with last three substituents.

Steric factors also play an important role in the formation of platina-cycloalkanes. Thus, 1,1,2-tetramethylcyclopropane fails to react with $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\eta\text{-C}_2\text{H}_4)]_2$ (228). Insertion generally occurs at the less substituted cyclopropane bond. However, in a few instances (when $\text{R} = n\text{-Hx}$, Bz , Ph , $o\text{-NO}_2\text{C}_6\text{H}_4$, $p\text{-MeC}_6\text{H}_4$, *trans*-1,2-diphenyl, or *trans*-1-methyl-2-*n*-butyl) (226,227), insertion at the most substituted bond has been observed. 1,2-Disubstituted cyclopropanes also give platinum(IV) metallacyclobutanes when treated with $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\eta\text{-C}_2\text{H}_4)]_2$ (Zeise's dimer) (229). *cis*-1-Methyl-2-*n*-butyl- and 1,1,2-trimethylcyclopropane on treatment with $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\eta\text{-C}_2\text{H}_4)]_2$ at room temperatures give olefin complexes (227,230,231). At -40°C , however, 1,1,2-trimethylcyclopropane yields the corresponding platinacyclobutane, which on warming to room temperature isomerizes to the (2,3-dimethyl-1-butene)metal complex (230,231). The observation of Brown *et al.* (228) that methylcyclopropane is inert toward $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\eta\text{-C}_2\text{H}_4)]_2$ was found to be incorrect (232,233).

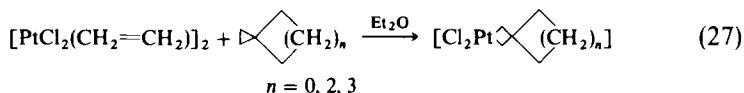
It is interesting to note that when the reaction of cyclopropane was carried out with either Zeise's complex anion $[\text{PtCl}_3(\text{CH}_2=\text{CH}_2)]^-$ in ethanol or $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\eta\text{-C}_2\text{H}_4)]_2$ in chloroform, dichloromethane, or ethanol the

propylene complex $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{CH}_3\text{CH}=\text{CH}_2)]_2$ was obtained (234). The latter, and the cyclopropane complex $[\text{PtCl}_2(\text{C}_3\text{H}_6)]_n$, can readily be inter-converted by passing cyclopropane or propylene, respectively, through their solutions [Eq. (26)].

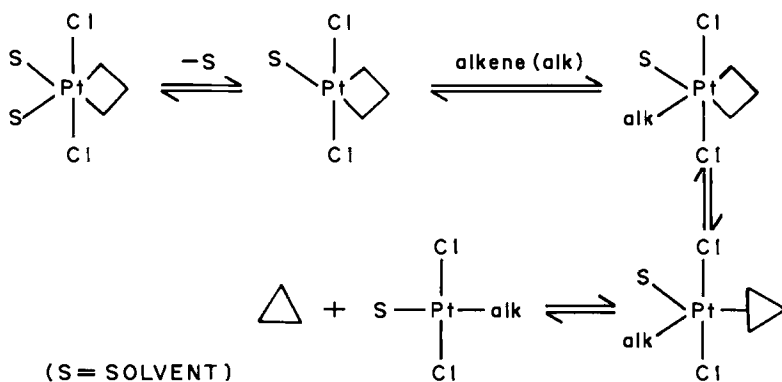


The kinetics of the reaction of arylcyclopropanes ($\Delta\text{—C}_6\text{H}_4\text{X}$ -4, X = H, Me, OEt) with either $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\eta\text{-C}_2\text{H}_4)]_2$ or $[\text{PtCl}_2(\text{CH}_2\text{CH}_2\text{CH}_2)]_n$ in THF has been studied (235,236). The reactions follow second-order kinetics, being first order in both platinum(II) complex and cyclopropane. The rates are accelerated in polar solvents, suggesting a polar intermediate. The reaction is believed to involve initial coordination of the cyclopropane to the platinum atom to give an "edge-complex," followed by ring opening to afford the platinacyclobutane with loss of alkene (Scheme 3).

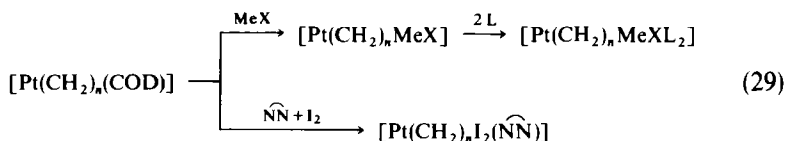
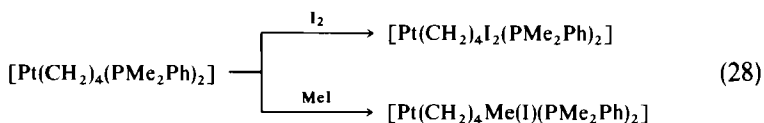
Reactions of spiroalkanes with $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\eta\text{-C}_2\text{H}_4)]_2$ in refluxing diethyl ether (237) yield platina spiroalkane complexes. In these reactions the site of insertion is the three-membered ring as the carbon-carbon bond remote from the spiro carbon, while the second ring is inert toward insertion [Eq. (27)]. However, 1,2-dicyclopropylethane gives a diplatinum derivative of the type $[\text{PtCl}_2\text{—}\text{CH}_2\text{—}]_2$ (226,227).



A general method for the preparation of higher homologs of platina-cyclobutanes involves the oxidative addition of halogen or alkyl halides on corresponding platinum(II) complexes [Eqs. (28) and (29)] (238–241). Inter-



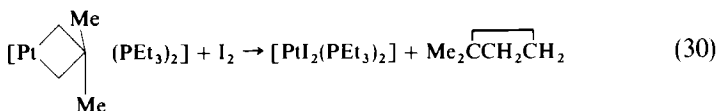
SCHEME 3



$n = 4, 5$; $\widehat{\text{NN}}$ = chelating nitrogen donor ligands

estingly, when the same reaction is carried out at room temperature with $n = 5$ and $\widehat{\text{NN}} = (\text{Me}_2\text{pz})_2\text{CH}_2$, the complex $[\text{PtI}_2(\widehat{\text{NN}})]$ is isolated rather than $[\text{Pt}(\text{CH}_2)_5\text{I}_2(\widehat{\text{NN}})]$ (242). Oxidation of $[\text{Pt}(\text{CH}_2)_5\text{L}_2]$ (L = tertiary phosphine) by bromine gives a mixture of compounds including $[\text{Pt}(\text{CH}_2)_5(\text{Br})_2\text{L}_2]$ (25–30%) (240).

Polymeric halogen-bridged platinacyclobutanes, like the analogous alkyl compounds, react with neutral nitrogen donor ligands to give monomeric complexes which are soluble in organic solvents, and can readily be characterized by spectroscopic techniques. Reactions of platinacyclobutanes with soft ligands such as CO, ER_3 (E = P, As, Sb) (223,225,243), dialkylsulfides, dimethylsulfoxide (243), cyanide, or iodide ions leads to reductive elimination of cyclopropane. These ligands can also displace cyclopropane from pyridine complexes, while the bipy or ethylenediamine adducts are stable toward these ligands (243). In contrast platinum(II) metallacyclobutanes are stable with soft ligands, although on oxidation cyclopropane is easily lost [Eq. (30)],



probably via a short-lived platinum(IV) species (244). Platinacyclopentane complexes containing tertiary phosphines are stable at room temperatures (238). The coordination chemistry of platinacyclobutanes is limited to hard bases of low trans effect such as pyridine.

Bulky nitrogen donor ligands such as 2-methylpyridine or 2,6-dimethylpyridine and weakly coordinating ligands such as methyl cyanide induce decomposition of platinacyclobutane complexes to give ylide or alkene complexes of platinum(II) (232). Complexes with oxygen donor ligands can rarely be isolated, although they exist in solution (235). However, 1,4-dioxane gives an isolable dimeric platinum complex (224). The oxygen or nitrogen donor ligands in monomeric platinacyclobutane complexes are labile and are often easily displaced by other nitrogen donor ligands (224,231,243,245).

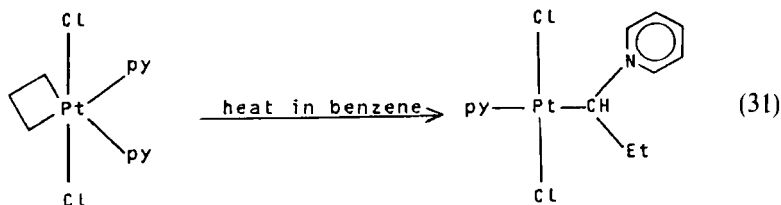
Photolysis of platinacyclobutanes gives cyclopropane, together with other products (246–248). Photolysis products of $[\text{Pt}(\text{CH}_2)_3\text{Cl}_2(\text{phen})]$ vary with conditions (247). In dichloromethane, for example, propene ($\sim 92\%$), cyclopropane ($\sim 7\%$), and ethylene ($\sim 1\%$) are formed. In presence of toluene or thiophenol in DMSO small amounts of propane (1 and 5%, respectively) are observed as gaseous products. In the presence of CBr_4 , 1,3-dibromopropane has been detected (247). A mechanism involving a platinum ion radical has been suggested (247,248). The photolysis of $[\text{Pt}(\text{CH}_2)_4\text{I}_2(\text{PMe}_2\text{Ph})_2]$ in CH_2Cl_2 yields ethylene ($\sim 70\%$) and but-1-ene ($\sim 30\%$). No deuterium incorporation in the gaseous products was observed when the reaction was carried out in $\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_5\text{CD}_3$. This, together with the absence of ethane or *n*-butane, indicates that free radical type intermediates are not formed. Ligand dissociation was responsible for the formation of but-1-ene, since in the presence of excess PMe_2Ph only ethylene was formed (247).

Pyrolysis of platinum(IV) metallacyclobutane complexes generally gives cyclopropane as one of the products (244,249,250). Pyrolysis of platinacyclobutane complexes containing the ligands pyridine, 4-methylpyridine, bipy, phen, or ethylenediamine gives mainly cyclopropane (75–80%) and propane whether the reaction is carried out in the solid state or in solution with the formation of platinum(II) complexes $[\text{PtCl}_2\text{L}_2]$ (249,250). A reversible dissociation of a ligand has been proposed for these reactions, since the rate of decomposition was markedly retarded by small amounts of free ligands. In the case of the ethylenediamine complex, the volatile products were identified as propene, cyclopropane, and hydrogen halides, together with small amounts of ethylenediamine (250). The involvement of a hydrido(π -allyl)platinum(IV) complex $[\text{PtH}(\text{X})\text{L}_2(\eta\text{-C}_3\text{H}_5)]^+$ for propene elimination has been proposed, this intermediate having been formed by a β -elimination reaction (250).

The thermal decomposition of $[\text{Pt}(\text{CH}_2)_4\text{I}_2(\text{PMe}_2\text{Ph})_2]$ gives $[\text{PtI}_2(\text{PMe}_2\text{Ph})_2]$ and but-1-ene. The reaction proceeds by ligand dissociation followed by β -elimination, and finally reductive elimination (238). The methylplatinum–metallacyclopentane complexes give a mixture of products depending on the nature of the ligands. Complexes containing nitrogen donor ligands such as py and bipy give methane, but-1-ene, and *cis*- and *trans*-but-2-enes. In contrast, tertiary phosphine complexes (PMe_2Ph or PMePh_2) decompose to give pent-1-ene as the major product, together with smaller quantities of isomeric pentenes (238) with the formation of $[\text{PtH}(\text{X})\text{L}_2]$. The first step was thought to be the concerted reductive elimination by cleavage of $\text{Pt}-\text{CH}_3$ and one of the $\text{Pt}-\text{CH}_2$ bonds to give pentylplatinum(II) species which undergo β -elimination of pent-1-ene to yield *trans*- $[\text{PtH}(\text{X})\text{L}_2]$. Interestingly, when $[\text{Pt}(\text{CH}_2)_4(\text{CF}_3)\text{I}(\text{PBu}_3)_2]$ was pyrolyzed, cyclobutane was the major product (240), and *trans*- $[\text{PtCF}_3\text{I}(\text{PBu}_3)_2]$ was formed predominantly rather than *trans*- $[\text{PtH}(\text{I})(\text{PBu}_3)_2]$. Similarly,

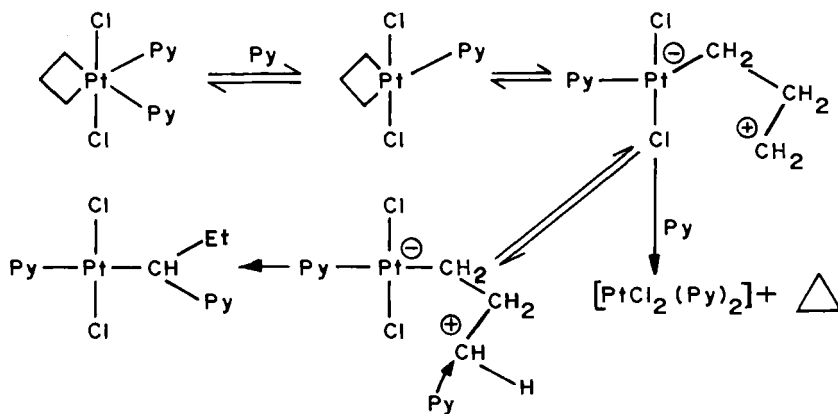
cyclopentane was obtained quantitatively when $[\text{Pt}(\text{CH}_2)_5(\text{Br})_2\text{L}_2]$ (L = a tertiary phosphine) was pyrolyzed for 17 hours at 120°C (240).

Chatt *et al.* (223) showed that refluxing benzene solutions of $[\text{Pt}(\text{CH}_2)_3(\text{Cl})_2(\text{py})_2]$ gave a yellow isomer, which was subsequently shown to be an ylide complex of platinum(II) [Eq. (31)] (251–253). This complex reacts with



chloroform to afford a platinum(IV) ylide complex. The crystal structures of both of these ylide complexes have been determined by X-ray diffraction methods (253). A kinetic study suggested that the isomerization involved an initial dissociation of pyridine, because the reaction was retarded by added pyridine, followed by nucleophilic attack of the dissociated pyridine at a carbon of the platinacyclobutane ring (254). During isomerization some *trans*- $[\text{PtCl}_2(\text{py})_2]$ and cyclopropane were also formed. Labeling experiments demonstrated that the isomerization involved a 1,3-H shift, and was believed to occur by an α -elimination mechanism (255). A suggested overall mechanism for the reaction is shown in Scheme 4.

Ring-substituted platinacyclobutanes give either olefin or ylide complexes, depending on the nature of the Lewis base and the ring. The pyridine complexes generally give ylides, whereas in the presence of acetonitrile olefin complexes form. However, platinacyclobutanes substituted on two carbon



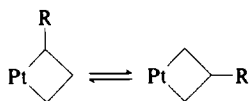
SCHEME 4

atoms of the ring give mainly olefin complexes (230,231). In both cases a mechanism involving β -elimination of a ring proton to form an intermediate π -allyl platinum hydride has been suggested. If in this intermediate the steric interactions are severe immediate reductive elimination of an olefin takes place, whereas the sterically nondemanding allyl persists long enough to allow attack by pyridine with subsequent ylide formation (230). Photolysis of platinum ylide complexes affords aldehydes (255). Platinum(II) and platinum(IV) ylide complexes react with carbon monoxide to give the corresponding Pt—(CO) ylide complexes (256).

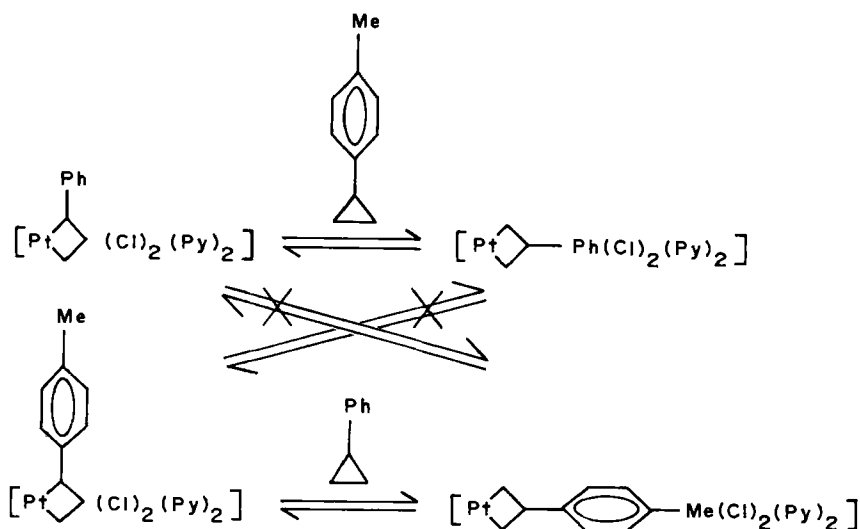
Thermolysis of deuterium-labeled substituted cyclopropane derivatives of platinum(IV) has been studied, and olefin formation has been found to be a β -hydrogen abstraction process, followed by reductive elimination (257). β -Hydrogen abstraction from the ring of the platinacyclobutane was favored over β -hydrogen abstraction from a methyl substituent at the α -position (257). However, Ling and Puddephatt (258) have recently proposed an α -elimination (1,3-H shift) mechanism.

Thermolysis of phenyl-substituted platinacyclobutanes give a mixture of phenylcyclopropane, propenylbenzene, and propylbenzene (259). Cathodic or chemical (sodium amalgam in acetonitrile at 0°C) reduction of [Pt(CH₂)₃-Cl₂(bipy)] gave the corresponding platinum(II) derivative [Pt(CH₂)₃(bipy)] (260). Reductive elimination of cyclopropane from platinacyclobutanes generally occurs with retention of stereochemistry about the ring, and a concerted mechanism involving an edge-complex intermediate appears to be operative (232,261,262).

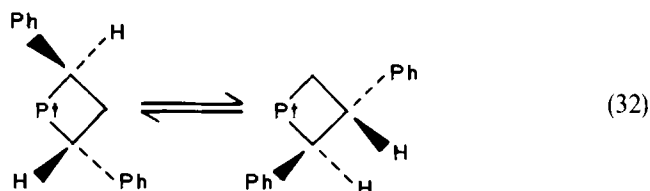
Substituted platinacyclobutanes in solution undergo facile skeletal isomerization reactions, and these occur in a stereospecific manner (299,232,262,263):



The ratio of the two isomers present in solution depends both on the nature of the R group and on the neutral ligand. When the platinacyclobutane ring carries an alkyl group the equilibrium is generally rapidly attained. However, with aryl substituents the isomerization is often slow and can be observed experimentally. The steric bulk of the R group appears to be important, since in case of the butyl- or hexyl-substituted derivatives the final product has the alkyl group exclusively on the central carbon atom. The isomerization has been shown to be intramolecular in nature, as no cross products are formed when a platinacyclobutane complex is isomerized in presence of a "second" cyclopropane (Scheme 5) (262). Furthermore, the isomerization occurs with

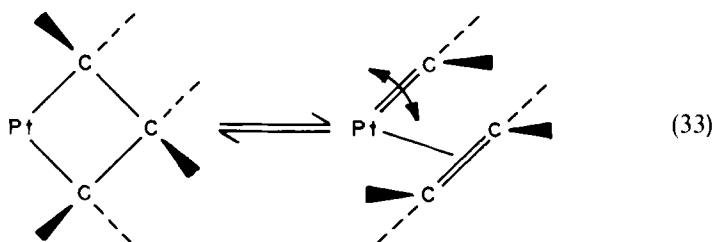


complete retention of stereochemistry [Eq. (32)]:



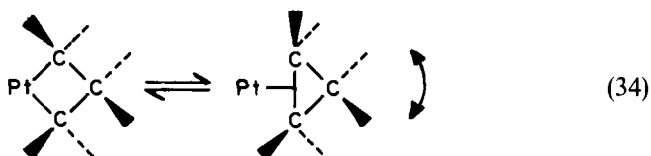
The isomerization is retarded by the addition of pyridine, but this effect does not operate when chelating nitrogen donor ligands are present such as bipy (259,262).

Different mechanisms have been proposed to explain the skeletal isomerization of platinacyclobutanes. A mechanism involving an alkene-carbene complex of platinum(II) has been considered in which the alkene can rotate and then form the isomerized platinacyclobutane [Eq. (33)]. However, ex-

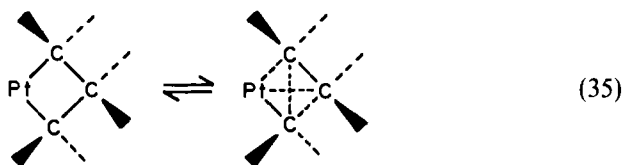


perimental observations do not support this mechanism. Ethylene (from platinacyclobutane complexes) and $\text{RCH}=\text{CH}_2$ (from substituted platinacyclobutane complexes; R = substituent in the ring such as Me, Ph) might be the expected products on pyrolysis of platinacyclobutane, but such products are seldom observed in significant yields (249,259). Second, if the carbene also rotates (as the evidence suggests) the stereochemistry of the ring is lost.

The second mechanism involves an "edge-complex" of platinum and a cyclopropane group [Eq. (34)] (245,261,262). Reductive elimination of cyclopropane promoted by ligand dissociation also gives an edge-complex which then undergoes an edge-to-edge migration followed by ring opening to yield the isomerized platinacyclobutane. A difficulty with this mechanism is the relatively high energy of the postulated intermediate.



The third mechanism proposed a concerted process in which C—C and Pt—C bond cleavage and reformation occur [Eq. (35)]. The intermediate resembles the carbene-alkene intermediate, mentioned earlier, except that complete rupture of a C—C bond never occurs (229,232,263,264). The retention of the stereochemistry of the ring and the absence of cross products support this mechanism. A fourth mechanism has recently been proposed by Wilker and Hoffmann (265) based on the activity and capability for polytopal rearrangement of the five-coordinate complex $[\text{Pt}(\text{CH}_2)_3(\text{Cl})_2(\text{L})]$.



Puckering in the rings of hydroxymethyl-substituted platinacyclobutane complexes has been studied by Puddephatt *et al.* (266). It has been observed that the puckering of the ring differs between the solid and solution states. Several platinacycloalkane complexes have been studied by X-ray diffraction methods (239,251–253,260,266,267). In all of them, platinum is bonded to the cyclopropane ring by σ bonds rather than coordination of the ring as an edge-complex. The platinum σ -bonded carbon atoms and the pyridine nitrogen atoms in $[\text{Pt}(\text{CH}_2)_3\text{Cl}_2(\text{py})_2]$ are essentially coplanar, the cyclopropane ring being oriented at 12.5° to this plane (252). The *cis*-pyridine ligands are arranged in a propellar like way around the platinum atom (Fig. 12).

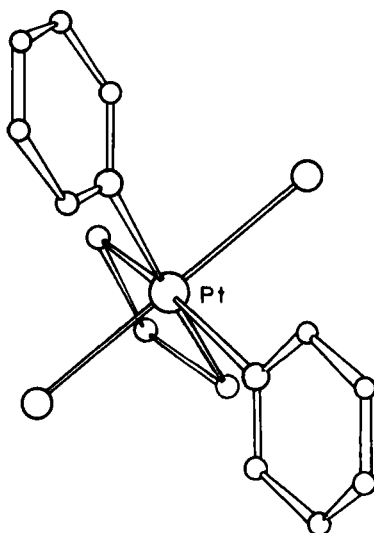


FIG. 12. Crystal and molecular structure of $[\text{Pt}(\text{C}_3\text{H}_6)\text{Cl}_2(\text{py})_2]$. [By permission from the Royal Society of Chemistry, N. A. Bailey *et al.*, *J. Chem. Soc., Chem. Commun.*, 396 (1966) (251).]

The crystals of $[\text{Pt}(\text{C}_3\text{H}_4\text{Ph}_2)\text{Cl}_2(\text{py})_2] \cdot 1/2\text{EtOH}$ are triclinic, space group $P\bar{1}$. Interestingly, there are two independent molecules in the unit cell which differ significantly in the observed geometries of the cyclobutane ring, although the attachment of the substituted cyclopropane to the platinum atom is basically the same in both molecules (267). In one molecule the angle subtended to platinum by the nitrogen atoms of the pyridine ligands is $92(1)^\circ$ and the plane of the phenyl rings is perpendicular to that of cyclopropane ring (Fig. 13b). In the other molecule the corresponding N—Pt—N angle is $82(1)^\circ$, and the planes of the phenyl and cyclopropane rings are not mutually perpendicular (Fig. 13a). The platinum atoms in both molecules have two

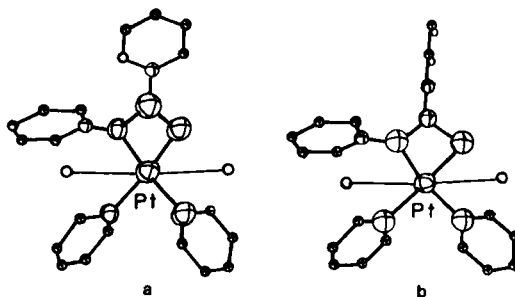


FIG. 13. Crystal and molecular structure of $[\text{Pt}(\text{C}_3\text{H}_4\text{Ph}_2)\text{Cl}_2(\text{py})_2] \cdot 1/2\text{EtOH}$. (a) Planes of the phenyl rings are not perpendicular to the cyclopropane ring. (b) A plane of one of the phenyl rings is perpendicular to the cyclopropane ring. [By permission from Elsevier Sequoia, S.A., J. A. McGinnety, *J. Organomet. Chem.* **59**, 429 (1973) (267).]

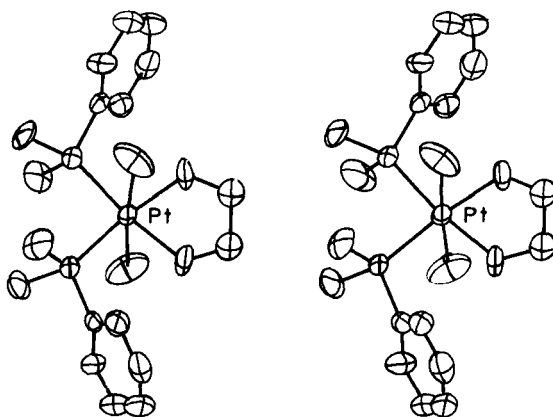
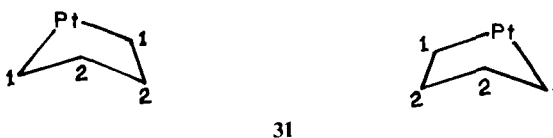


FIG. 14. Stereoview of the molecular structure of $[\text{Pt}(\text{CH}_2)_4\text{I}_2(\text{PMe}_2\text{Ph})_2]$. [Reprinted with permission from *Inorg. Chem.* **15**, 2997. Copyright (1976) American Chemical Society (239).]

trans chlorine atoms at axial positions. Carbon 2 of the cyclopropane ring is considerably farther away from platinum (267) and slightly displaced from the equatorial plane.

The complex $[\text{Pt}(\text{CH}_2)_4\text{I}_2(\text{PMe}_2\text{Ph})_2]$ has a twofold axis through platinum atom. The disorder observed in the butanediyl ring is a result of the two central carbon atoms alternating between the two forms (**31**) (239). This puckering of the ring relieves crowding of the hydrogen atoms on adjacent carbon atoms, and the two conformations are equivalent (Fig. 14).



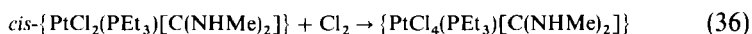
VIII

OTHER COMPOUNDS

Recently a few papers have appeared which describe platinum(IV) carbonyl complexes (268–272). The pentanuclear cluster, $[\text{Pt}(\text{CO})_2]_5$, in the presence of ferric and halide ions in water, yields the pentacoordinate platinum(IV) carbonyl compound $[\text{Pt}(\text{H})_2\text{X}_2(\text{CO})]$ which in aqueous chloride solution picks up another ligand to give six-coordinate anionic complexes $[\text{Pt}(\text{H})_2\text{X}_3(\text{CO})]^-$. The latter may be isolated as its tetraalkylammonium salt. In the presence of ferric ions the five-coordinate complexes $[\text{Pt}(\text{H})_2\text{X}_2(\text{CO})]$

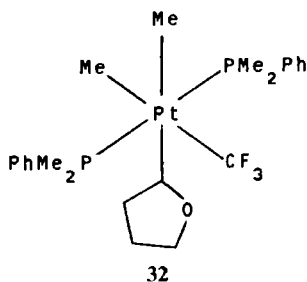
catalyze the oxidation of carbon monoxide in aqueous solution, and the rate is dependent on ferric ion concentration and decreases as the halide increases in atomic number (273,274). An X-ray analysis of $[\text{Et}_4\text{N}][\text{Pt}(\text{H})_2\text{Br}_3(\text{CO})]$ shows an octahedral configuration, with *trans*-hydride ligands around the platinum atom (271). The carbonyl complexes $[\text{PtX}_5(\text{CO})]^-$ ($\text{X} = \text{Cl}, \text{Br}$), produced in solution by halogenation of $[\text{PtX}_3(\text{CO})]^-$, have been studied by IR and ^{13}C -NMR spectroscopy (272).

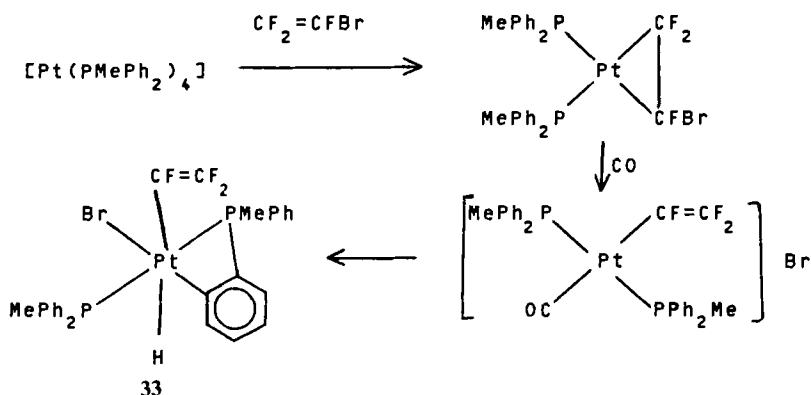
Platinum(IV) carbene complexes are also known, but their properties have not been investigated in detail. Oxidative addition of chlorine to platinum(II) carbene complexes affords the corresponding platinum(IV) compounds when the carbene ligand contains only alkyl groups [Eq. (36)] (275,276). When the



ligand contains a phenyl group, chlorination of $\{\text{PtCl}[\text{C}(\text{NHMe})(\text{NHPh})](\text{PEt}_3)_2\}\text{ClO}_4$ results in 2-metallation and 4-chlorine substitution of the phenyl group (275), as shown by the X-ray analysis of $\{\text{Pt}[\text{C}(\text{NHMe})(\text{NHC}_6\text{H}_3\text{Cl})]\text{Cl}_2(\text{PEt}_3)_2\}\text{ClO}_4$ (275,277). The molecule shows a slightly shorter than expected $\text{Pt}-\text{C}_{\text{carbene}}$ bond [$0.048(21) \text{ \AA}$] indicating little π -backdonation. Interestingly the oxidation of *trans*- $\{\text{PtMe}(\text{PEt}_3)_2[\text{C}(\text{OMe})\text{Me}]\}\text{PF}_6$ with iodine in methanol gives the platinum(II) iodo complex, *trans*- $\{\text{PtI}(\text{PEt}_3)_2[\text{C}(\text{OMe})\text{Me}]\}\text{PF}_6$, probably via a platinum(IV) intermediate (278). Methyl iodide oxidatively adds to $[\text{PtMe}(\text{PMe}_2\text{Ph})_2(\text{COCH}_2\text{CH}_2\text{CH}_2)]\text{PF}_6$ to give the corresponding platinum(IV) carbene complex, $[\text{PtMe}_2(\text{I})(\text{PMe}_2\text{Ph})_2(\overline{\text{COCH}_2\text{CH}_2\text{CH}_2})]\text{PF}_6$ (68).

Oxidative addition of a carbene precursor to a platinum(II) complex generates platinum(IV) carbene complexes (279,280). Thus, (chloromethylene)-dimethylammonium chloride, $[\text{NMe}_2(\text{CHCl})]\text{Cl}$, reacts with *cis*- $[\text{PtCl}_2-(\text{PEt}_3)(\text{CH}_2=\text{CH}_2)]$ to afford $[\text{PtCl}_4(\text{PEt}_3)(\text{C}(\text{H})\text{NMe}_2)]$. Although platinum(IV) acetylene complexes have not yet been reported, the alkyne $\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{OH}$ reacts with $[\text{PtMe}_2(\text{CF}_3)(\text{PMe}_2\text{Ph})_2(\text{acetone})]\text{PF}_6$ in acetone to yield a platinum(IV) carbene complex **32** which is formed probably via a very reactive carbonium ion intermediate (281).

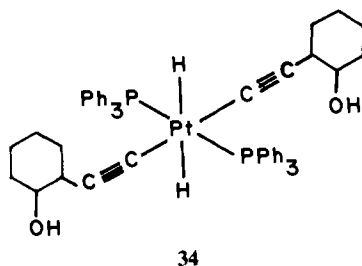




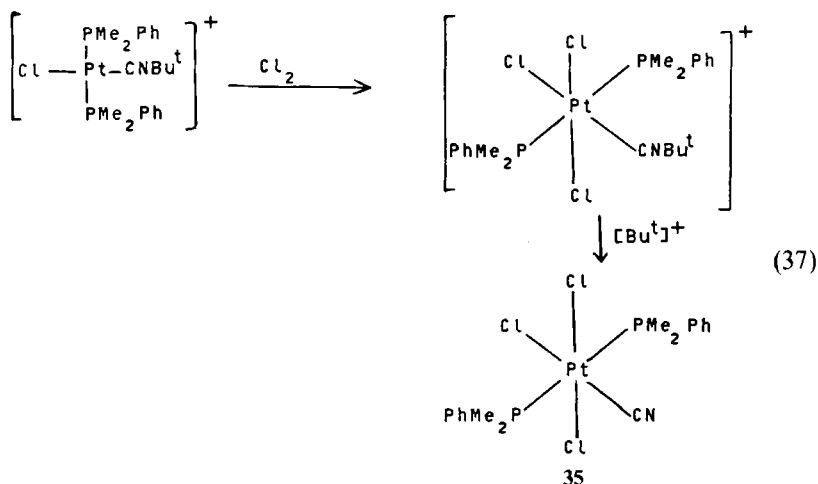
SCHEME 6

The complex $[\text{Pt}(\text{MePh}_2\text{P})_4]$ reacts with bromotrifluoroethylene to give $[\text{Pt}(\text{CF}_2=\text{CFBr})(\text{PMePh}_2)_2]$, which on treatment with CO affords a platinum(IV) complex (**33**) (282) where one of the phenyl groups of the phosphine ligand is ortho metallated (Scheme 6). The formation of the platinum(IV) complex probably involves an intermolecular oxidative addition reaction by a cationic platinum(IV) carbonyl, formed by nucleophilic attack of CO on the platinum(0) olefin complex.

The reaction of $[\text{Pt}(\text{PPh}_3)_4]$ with 1-ethynylcyclohexanol gives the dihydridoplatinum(IV) acetylide for which the structure **34** has been proposed (283).



The oxidative addition of chlorine to the neutral and cationic platinum(II) isocyanide complexes yields the corresponding platinum(IV) isocyanide complexes, $[\text{PtCl}_4(\text{RNC})_2]$, $[\text{PtCl}_4(\text{PMe}_2\text{Ph})(\text{RNC})]$, $[\text{PtCl}_3(\text{PMe}_2\text{Ph})_2(\text{RNC})]^+$, and $[\text{PtCl}_2(\text{PMe}_2\text{Ph})_2(\text{RNC})_2]^{2+}$ ($\text{R} = \text{Me}, \text{Bu}', \text{c-Hx}, \text{p-tolyl}$). The cationic *tert*-butylisocyanide complexes (284) readily lose the Bu' group at room temperature to give corresponding cyano complexes (**35**) [Eq. (37)].



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Sodium, Potassium, Rubidium, and Cesium: X-Ray Structural Analysis of Their Organic Compounds¹

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I

INTRODUCTION

Organolithium compounds (*1*), commonly but somewhat misleadingly referred to as "carbanions," have been studied intensively in recent years. As much of the chemical behavior of these polar organometallic species cannot be understood without a knowledge of the location of the metal atom and the degree of aggregation and solvation, elucidation of these important details has become of increasing interest. Reactions, for example, not only involve alkali counteranions; they often are induced at the metal center (*2*).

Quite different investigative techniques are being employed: NMR,² UV, MS, or colligative measurements. Perhaps the most powerful methods are proving to be theoretical calculations and X-ray analysis (*1*). Even though these correspond to the gas or solid phases, respectively, the structures often are expected to resemble those in solution. The fascinating information these structures reveal refine the chemist's way of thinking about his synthetic

¹ Dedicated to Prof. Erwin Weiss on the occasion of his sixtieth birthday.

² List of abbreviations: NMR, nuclear magnetic resonance; Me, methyl; Et, ethyl; ^tBu, *tert*-butyl; *n*Bu, *n*-butyl; Ph, phenyl; tmeda or TMEDA, *N,N,N',N'*-tetramethylethylenediamine; pmdta or PMDTA, *N,N,N',N',N''*-pentamethyldiethylenetriamine; thf or THF, tetrahydrofuran; dme or DME, dimethoxyethane; diglyme, di-2-methoxyethyl ether; 12-c-4, 1,4,7,10-tetraoxacyclododecane (12-crown-4); 15-c-5, 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5); 18-c-6, 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6); db-18-c-6, 1,4,7,14,17,20-hexaoxa[7.7]orthocyclophane (dibenzo-18-crown-6); dabco, 1,4-diazabicyclo[2.2.2]octane; cot or COT, cyclooctatetraene; cod or COD, cyclooctadiene; cp, cyclopentadiene; salen, *N,N'*-ethylenebis(salicylideneiminato); acac, acetylacetonato; hfacac, hexafluoroacetylacetonato.

intermediates. Many insights can be gained by knowing the precise locations of atoms in molecules.

Compared to organolithium derivatives, however, much less attention has been paid to the corresponding organometallic compounds of the higher alkali metals sodium, potassium, rubidium, and cesium (3). (Francium, an element with no stable isotopes, is not considered here at all.) Theoretical calculations are an increasingly important source of structural and energetic information; however, relatively few calculations have been reported on organosodium compounds (4) and hardly any involving the heavier alkali metals. This situation is likely to change rapidly in the future, since the remarkable structures indicated by calculations on lithium compounds (5) have focused attention on their heavier metal counterparts.

The enhanced reactivity of the organometallic compounds of the heavier alkali metals is a desirable asset but also may lead to ready thermal decomposition. The lack of solubility in hydrocarbon media adds to the manipulative difficulties. Such compounds are rarely isolated, and their heterogeneous suspensions have not been able to compete with universal reagents like *n*BuLi/hexane for synthetic applications (3). For this reason, there has been relatively little interest in the X-ray structures of organic derivatives of the heavier alkali metals. While well over a thousand Na, K, Rb, and Cs structures are found in the Cambridge Crystallographic Data Base (6), the vast majority of these involve heteroatom-solvated atoms, and only a few compounds show metal-carbon contacts. However, the recent burst in activity in lithium structural chemistry (1) stimulates interest not only in the organic chemistry of the higher alkali elements but also in their structures.

In this article, we summarize the published X-ray investigations of organometallic compounds of Na, K, Rb, and Cs. We emphasize the structure-determining factors and, wherever possible, the trends within the first group including lithium. Organometallic molecules are defined as having metal-carbon contacts or closely related structures. Only those structures from the Cambridge Crystallographic Data Base (6) which might be termed to be "organometallic" in this restricted sense are presented, although representative examples of related compounds are included in Section V. Enolates illustrate systems which are obviously organic, but contain metal-heteroatom rather than metal-carbon contacts. These and similar compounds are included, but phenolates, for example, are not. The latter possess little "carbanionic" character and generally do not undergo C-alkylation. Similarly, compounds where alkali metal cations are merely solvated by monodentate, polydentate, or crown ether-type ligands are not examined exhaustively. The literature was reviewed systematically through 1984, but many structures through 1985 also are reported.

Few investigators have concentrated their research on the structures of the entire family of alkali metal compounds. The principal contributor to this area has been E. Weiss, Hamburg, who reported not only all the methylalkali structures but those of most other simple systems as well.³ We dedicate this review to him. The groups of C. Krüger and K. Jonas at the MPI, Mülheim an der Ruhr, have determined structures of transition metal compounds (7). In Alabama, J. Atwood has studied many of the group 13 mixed metal compounds (8). At Nijmegen, J. H. Noordik, E. de Boer, and co-workers have investigated radical anions of aromatic hydrocarbons (9). In the late 1960s, many structures of "carbanions" derived from quite acidic carbon compounds have been revealed by Klewe and Grigor'eva and their co-workers.⁴ General coordination chemistry of alkali ions with organic ligands, especially of polydentate chelated compounds, has long been of major interest; for excellent reviews, see Ref. 10.

II

FACTORS DETERMINING ORGANOALKALI STRUCTURES

In general, organoalkali compounds may be written as $[RM_m \cdot L_n]_k$, where R represents an organic group, M the alkali metal, L additional donor ligand(s), and k the degree of aggregation. All these components in the structure are important and will be discussed separately.

A. The Carbanion: Charge Localization (4c, 11)

What are the structures of the free anion, e.g., of the methyl anion? Basic molecular orbital considerations would suggest strong pyramidity for the system due to double occupancy of the $3a_1$ -orbital given in Fig. 1. As the pyramidal inversion barriers of the isoelectronic species, H_3O^+ and NH_3 , are 1 and 6 kcal/mol, respectively, one expects the trend to continue and a higher value for CH_3^- . Indeed, this trend is indicated by 6-31G* *ab initio* calculations, which give values of 1.7, 6.5, and 13.0 kcal/mol, respectively (12). The geometries reflect these barriers. The oxonium ion is nearly planar ($\angle HOH = 113.1^\circ$ at 6-31G*), whereas the HNH angle in ammonia (107.2°) and the HCH angle in the methyl anion (101.8°) are both smaller with this

³ For leading references, see Refs. 52, 53, 56-61, 65, 77, 80, 81, 136-138, 141, 144-146, 152. A review of his work will be available in the near future.

⁴ For references, see Table VII.

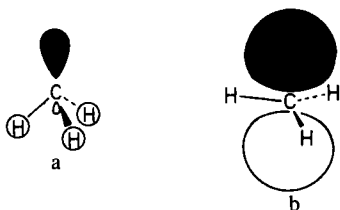


FIG. 1. $3a_1$ molecular orbital of the methyl anion as described without (a) and with (b) diffuse augmented basis sets.

basis set (12a). While these results for OH_3^+ and NH_3 are reasonably accurate, those for CH_3^- are artifacts of the too limited mathematical description. Higher level calculations which are suitable for anionic species give quite a different picture (13). Larger basis sets which include diffuse functions give a CH_3^- inversion barrier of only 1.5 kcal/mol ($\angle \text{HCH} = 109.0^\circ$) (14). The most recent calculation, which used multiconfigurational wave functions, even predicts CH_3^- to be planar (15)!

The reasons for these deviations from simple expectations are easily understood. The experimental electron affinity of the methyl anion is only 1.8 ± 0.7 kcal/mol (16,17). This means that the outer electron is barely bound and resides in a very large (diffuse) orbital rather far from the carbon nucleus. Hence, this electron has little influence on the molecular geometry which thus more nearly resembles that of $\text{CH}_3\cdot$ (planar) (17). Other simple alkyl anions (ethyl, isopropyl, *tert*-butyl, etc.) are indicated to have negative electron affinities; i.e., they are not stable toward electron loss 17a. Hence, they are not expected to be observable as long-lived species in the gas phase and, in this sense, can be said not to exist.

Let us now consider the effect of an approaching counterion. Its electrostatic field will polarize the loosely bound electron density of the anion toward the positive charge, but this does not necessarily lead to covalent bonding. This localization of electron density in the region between cation and anion will be more pronounced when cation-anion distances are shorter. A redistribution of the electron density within the occupied MOs of the organic moiety will occur, and diffuse functions will be much less populated. Due to this *charge localization*, geometries will deviate more and more from that of the free anion and resemble more those expected on the basis of classic structural considerations. Methyl groups in alkali metal compounds are pyramidal, for example. In addition, the HCH angles in CH_3Li (106.3°) and in CH_3Na (107.5°) are calculated (6-31+G* basis set) to have values appreciably smaller than tetrahedral (18). *Ab initio* data for sodium compounds are generally more in accord with those of the free anion than are data for lithium compounds (18). Thus, due to increasing carbon-

metal bond lengths, "more ionic" geometries should be observed for compounds of the heavier alkali metals. Organopotassium structures already will approach those of the unpaired free anion, whereas lithium compounds exhibit substantial distortions.

This trend can be illustrated by several crystal structures. A nice example is provided by triphenylmethyl derivatives. The free anion in the solvent-separated ion pair $[\text{Li}(12\text{-crown-4})_2][\text{CPh}_3] \cdot \text{thf}$ (19) is planar with respect to the central carbon and α -carbons of the three phenyl groups. In the sodium contact ion pair $[\text{Na}(\text{tmeda})][\text{CPh}_3]$ (20), a slight distortion from planarity is observed; the central carbon is displaced (0.4 pm) toward the cationic center. In the lithium contact ion pair $[\text{Li}(\text{tmeda})][\text{CPh}_3]$ (21) this out-of-plane displacement is quite large (12 pm). The cation provokes a redistribution of anionic charge. The electrostatically favorable localization on the central atom induces pyramidalization.

The countercation influences not only geometries. Anion stabilizing (or destabilizing) substituent effects are reduced significantly in the corresponding organometallic compounds (4a), again following the order within the group, $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$. Carbanionic rearrangements support this conclusion (22). Since charge delocalization stabilizes the transition state and is inhibited by the smaller cations, considerable rate enhancement is found in going along the counterion series from Li to Cs. Similarly, as delocalization often leads to colored species, deepening of colors is often reported as the cation is changed down the column.

B. The Cation

Almost all physical properties of the alkali elements show the most pronounced regularities and the least scatter among elements of the same group in the periodic system (23). Properties of the organoalkali compounds follow mass/size influences as well. However, on this basis certain groupings are apparent: potassium and rubidium derivatives markedly resemble those of cesium, while sodium and lithium are more closely linked (compare Table I).

Atomic radii cannot be assigned without ambiguity. Consistent sets can be based on the diatomic distances, the separations of atoms in the metal, those in crystals, etc. For any given set the relative differences between any two of the metals are approximately constant. This relation may be used to predict a complete set of partly unknown data by extrapolation from available values, e.g., for bonding radii from computed data of organoalkali monomers. Subtraction of the single bond radius of carbon (0.77 Å, one-half the C—C bond length in alkanes) from 6-31G* *ab initio* bond lengths in alkyl-metal compounds (Li, 2.00 Å; Na, 2.34 Å) yields bonding radii for these elements

TABLE I
 PROPERTIES OF THE ALKALI METALS

	Li	Na	K	Rb	Cs
Relative atomic mass	6.94	22.99	39.10	85.47	132.91
Electronegativity					
Allred–Rochow ^a	0.97	1.01	0.91	0.89	0.86
Sanderson ^b	0.670	0.560	0.445	0.312	0.220
Ionization potential ^c (eV)	5.390	5.138	4.339	4.176	3.893
Electron affinity ^d (eV)	0.611	0.539	0.497	0.490	0.470
1/2 Bond length in M ₂ ^e (Å)	1.34	1.54	1.96	2.12	2.28
Metallic radius ^e (Å)	1.52	1.86	2.27	2.48	2.65
Bonding radius, ^f X-ray (Å)	1.48	1.83	2.21	2.39	(2.6) ^g
Bonding radius, ^f <i>ab initio</i> (Å)	1.25	1.6	(2.0) ^g	(2.15) ^g	(2.35) ^g
Ionic radius, ^h <i>r</i> _i (Å)	0.60	0.95	1.33	1.48	1.69
1/ <i>r</i> _i ⁱ (1/Å)	1.67	1.05	0.75	0.68	0.59
Δ <i>r</i> ^j (Å)	0.35	0.4	0.15	0.2	—

^a E. J. Rochow, A. L. Allred, *J. Inorg. Nucl. Chem.* **5**, 264 (1958).

^b R. T. Sanderson, "Polar Covalence." Academic Press, New York, 1983.

^c A. F. Hollemann and E. Wiberg, "Lehrbuch der Anorganischen Chemie." de Gruyter, Berlin, 1985.

^d H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data* **4**, 539 (1975).

^e Calculated from shortest distances in bcc crystals of the elements.

^f See text for evaluation.

^g Extrapolated.

^h L. Pauling, "The Nature of the Chemical Bond." Cornell Univ. Press, Ithaca, New York, 1960.

ⁱ Representing the electrostatic interaction energy of two opposed charges at *r*_i.

^j Approximate radius difference to the succeeding element.

(Li, 1.23 Å; Na, 1.57 Å), which may be extrapolated to the other metals (K, 2.0 Å; Rb, 2.15 Å; Cs, 2.35 Å).

X-Ray analysis-based bonding radii may be evaluated similarly. Table V (page 186) contains average bond length data for several classes of metal–carbon contacts. Again, differences between values for any pair of metals are nearly equal among the classes. Subtraction of the bonding radius of carbon from average bond lengths of monohapto-bonded species (alkyl, alkenyl, alkynyl, benzyl alkali compounds) defines the data compiled in Table I. Due to solvation and aggregation, these are about 0.2 Å larger than corresponding *ab initio* values for gaseous monomers.

1. Ionicity

The nature of carbon–lithium bonding once was controversial. As will be discussed below, the exceptional physical properties of lithium compounds

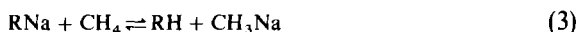
(e.g., volatility and solubility in organic solvents) led to the erroneous conclusion that the bonding was covalent. The observation of ^6Li – ^{13}C and ^7Li – ^{13}C NMR couplings in some organolithium compounds also suggest at least some covalent character (24,67). The unusual structures of lithium compounds were interpreted in terms of multicenter covalent bonding involving delocalized molecular orbitals over several atomic centers. On the other hand, the very high dipole moment (6 D) of CH_3Li [calculated and observed in a matrix (25)] indicates a high ionic character of the C—Li bond [the dipole moment of CH_3F is only 1.82 D (26)]. After a detailed study, Lipscomb concluded (27) that CH_3Li has about 60% ionic character. However, this, like earlier estimates, was an educated guess. Schiffer and Ahlrichs also found (28) that the C—Li bond, while predominantly ionic, had significant covalent contributions.

The ionic character of bonds is not easy to determine. Mulliken population analysis (29), often used for *ab initio* data, is known to have total deficiencies for ionic systems (30). Not only are the results very basis set dependent, but electrons “belonging” to one element are assigned to another. The ionic character is underestimated. These deficiencies have largely been overcome by more recent treatments. The integrated spatial electron populations of Collins and Streitwieser (31) indicate 79.7% ionic character in CH_3Li . The natural population analysis of Reed, Weinstock, and Weinhold (32) gives an essentially identical value (80.5%, also 6-31G*). The same method gives the following charges on the alkali metals [6-31G* (33)]: vinyl lithium, +0.857; lithioacetylene, +0.899; methyl lithium dimer, +0.869; η^3 -allyl lithium +0.893.

Although the bonding always is predominantly ionic, the degree of covalent character decreases as expected with the carbon hybridization ($sp^3 > sp^2 > sp$), with π bonding, and with aggregation. Finally, the best estimates can be obtained from Bader's charge density analysis, which indicates a lithium charge of +0.90 in CH_3Li (34), and from natural population analysis. By using a large basis set with diffuse orbitals (6-311 + G*), a lithium charge of +0.878 in CH_3Li is obtained. On the basis of such treatments, the C—Li bond is indicated to be 80–90% ionic. The somewhat lower degree of ionic character (79.6%, 6-31 + G*) in CH_3Na is unexpected but is in line with the Allred–Rochow electronegativities. Comparable or greater ionicities are expected for the organometallic compounds of the other alkali metals.

This conclusion can be reached in other ways. The *ab initio* dimerization energies of a set of LiX molecules could be reproduced with remarkable accuracy by a simple coulombic point charge Li^+X^- model (35). The complexation energies of LiX molecules ranging from LiF to Li_2 with water and ammonia are surprisingly constant (36); the predominately electrostatic nature of the interaction is responsible. Finally, the stabilization energies,

related to CH_3^- , of a set of carbanions [Eq. (1)] can be compared with corresponding data for the same set of lithium [Eq. (2)] and sodium derivatives [Eq. (3)] (11a,b). The plot of the data from Eqs. (1) and (2) gives a slope of 0.74, that for Eqs. (1) and (3) a slightly larger value of 0.81 (3-21G//3-21G). These are rough measures of the degree of ionic character in the organolithium and organosodium compounds, respectively.



In summary, lithium compounds are essentially ionic; most structural features can be deduced from electrostatic considerations. Radius relations ($1/r$) should provide useful approximations in order to discuss some structural details. However, the small covalent contributions to bonding may be significant, e.g., on the couplings observed in NMR spectra. Sodium compounds are similar. For potassium, rubidium, and cesium the ionic description will hold even better. Carbon-metal bond energies [~ 45 kcal/mol in CH_3Li , (28)] will decrease in the order Li to Cs; the electrostatic attractive interactions become weaker when the distance between the ions increases.

2. Coordination

The environment of the small lithium cation is governed primarily by steric factors. The most common coordination number is four, but much larger values may be found with polydentate ligands (1). As the bonding is mostly electrostatic with very little charge transfer, "electron counting" plays no role in determining the coordination numbers of alkali metal cations. The larger alkali ions prefer higher coordination numbers. Sodium tends toward five and six, even though both higher and lower numbers are observed as well. Potassium, rubidium, and cesium often choose eight-coordinate situations; low coordination numbers are not found (3,10) (compare Tables VII-XII).

Hence, structures deviating from known organolithium examples are to be expected even when the stoichiometry is the same. The pronounced structural influence of coordination numbers, i.e., ion size, has long been known: in homologous series the same space groups are often observed for K, Rb, and Cs compounds, whereas those involving Na (often) and Li (generally) deviate. This is illustrated by many inorganic compounds (37). Similarly, in crown ethers or cryptands a larger coordination sphere typically favors ions like potassium, whereas sodium and especially lithium ions often are restricted to only some of the sites or are bound more effectively by ligands with fewer heteroatoms (10,38).

3. Bridging

Multihapto interactions between a metal cation and an anion largely depend on relative size of both partners (39). For a given π system relative stabilities and geometries of the ion pairs will differ for cations of different size (Fig. 2). Rubidium and potassium compounds of the cyclooctatetraene dianion (40–42) may serve as examples of the first type. For a corresponding lithium compound a similar η^8 alternative would be unfavorable and distortions to lower symmetry and anticipated (type 2).

Electrostatic point charge models may be used to predict cation locations above a delocalized anionic moiety (43a). Often different relative stabilities of various possible positions are found since these depend differently on interchange distances ("haptotropic search," Refs. 43b–e). The different structures of fluorenyllithium and -potassium serve as an illustration (Fig. 3a). The free fluorenyl anion possesses a maximum charge density at the 9 position. The small lithium cation in fluorenyllithium \cdot bisquinuclidine (44) interacts with this site; the charge localization which develops stabilizes this position even more. The short Li—C-9 distance disfavors the alternative location over the center of the formal cyclopentadienyl system if further ligands are present.

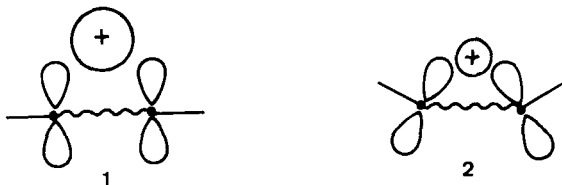


FIG. 2. Effect of alkali ion size on the bridging in delocalized π systems.

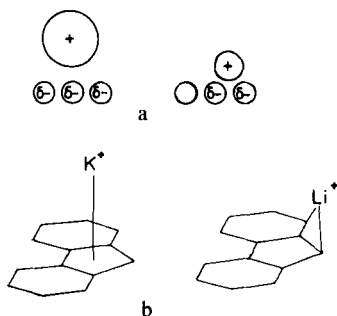


FIG. 3. (a) Alkali ions of different size may favor different positions above a delocalized carbanion. The larger cation prefers interactions with many centers; the smaller cation interacts with selected centers, inducing charge localization. (b) Bonding geometries in fluorenyllithium and -potassium.

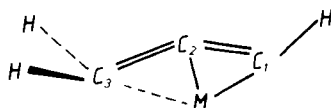


FIG. 4. *Ab initio* calculated geometries of allenyl alkali monomers.

Instead, the ortho position of one annelated benzo group, which shows the greatest remaining partial anion charge, is involved in lithium coordination. For the larger and less charge localizing potassium ion in $\text{KC}_9\text{H}_9 \cdot \text{tmeda}$ (45) multihapto bonding prevails (Fig. 3b).

Note, however, that energy surfaces for metal cations above a delocalized anionic system occasionally are quite flat (5,46) and level off with increasing cap-ring distance even more. Several different metal cation locations may exist for some species, even for the same compound (46b).

For some cases, bridging may be viewed as "intramolecular π electron solvation": One or more of the metal coordination sites are occupied by a neutral olefinic system. As solvation energies generally decrease in the order Li^+ to Cs^+ , bridging will be most pronounced for lithium compounds.

Allenyl alkali compounds illustrate this nicely. Both *ab initio* data (on the monomers) and X-ray structures are available. Vinyl lithium and -sodium monomers possess regular olefinic structures (18). However, introduction of a cumulenenic double bond leads to highly distorted, bridged structures in the allenic compounds (47) (Fig. 4). These geometries are not consistent with appreciable contributions from propargyl-type resonance structures. The two $\text{C}=\text{C}$ bonds are nearly equal in length and do not really differ in the theoretical and experimental structures. The alkali metal cations, while nearly equidistant to C-1 and C-2, are about 0.4 Å farther away from C-3. Further bending of the carbon skeleton, which would bring C-3 closer to the lithium cation, is resisted by the stiffness of the system. In the allenylsodium monomer, this bending is less pronounced (167° for Na versus 161° for Li) due to the greater metal carbon distances. Solvation in the crystal structures has a similar effect as it competes with the interaction of the cation with the allenyl anion moiety. The carbon-metal distances increase, and the CCC angles widen to 166° in the allenyllithium (1,48) and to 173° in the allenyl sodium derivative (49). The latter approaches the calculated value for the allenyl anion itself, 176° (6-31 + G*) (50).

C. Aggregation

Aggregation is of particular importance in lithium chemistry (1). In donor solvents, dimers and tetramers are typical, and they may be involved in temperature-dependent equilibria. Other compounds (e.g., alkali alcoholates,

alkali halides, organocopper compounds) can participate in these equilibria to form mixed aggregates. The nature of the carbanion is important; steric hindrance or charge delocalization favor monomeric aggregates. The clusters do not form rigid frameworks but undergo internal redistributions. Solid state structures seem to be reasonable models for solution behavior, although aggregation numbers in some cases are higher in the solid.

1. Solvation Dependence

Aggregation of organoalkali compounds is essentially electrostatic; two or more $M-C$ bond dipoles interact mutually with one another. Coordinating solvents introduce competing interactions, which tend to stabilize smaller aggregates preferentially. Ether-solvated phenyllithium is tetrameric in the solid state (51), dimers are formed in the presence of TMEDA (52), and monomers on PMDTA chelation (53); the coordination number of lithium remains four. Similarly, polymeric dipotassium cyclooctatetraenide·**diglyme** (40) is converted to an ion pair structure by further diglyme coordination (42).

Aggregation energies can be very large; they are largest for dimerization and fall off with increasing number of steps. Solvation energies can then become competitive. A good example is provided by $t\text{BuC}\equiv\text{CLi}$, which in principle could form the two-dimensional sheetlike arrays found for $\text{HC}\equiv\text{CM}$ species. However, the dodecamer is the largest aggregate observed (54,55). The four THF molecules evidently help to arrest further association (Fig. 5). [Under other conditions, the same compound forms a tetramer, $[t\text{BuC}\equiv\text{CLi}\cdot\text{thf}]_4$ (54).]

2. Ion Size Dependence

Dimerization energies of alkali halides in the gas phase (35) are presented in Table II. In accordance with electrostatic considerations, the largest values are found for the association of lithium compounds. Substitution of halide anions

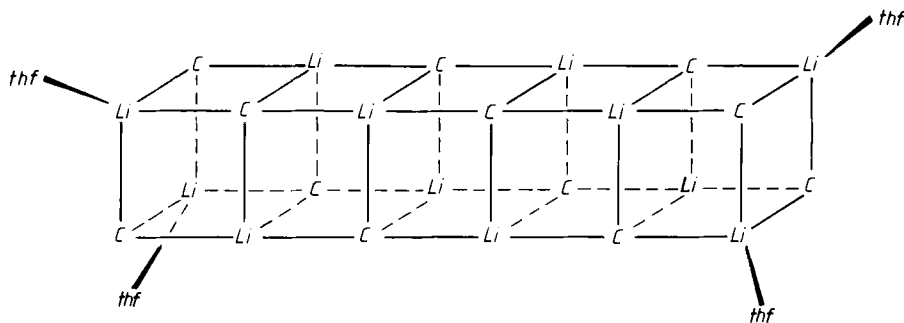


FIG. 5. Idealized carbon-lithium skeleton of the $[t\text{BuC}\equiv\text{C-Li}]_{12}\cdot(\text{thf})_4$ dodecamer.

TABLE II
 DIMERIZATION ENERGIES OF ALKALI HALIDE
 MOLECULES^a

	F	Cl	Br	I
Li	60.4	49.3	47.6	43.3
Na	61.2	50.0	43.9	44.2
K	49.9	45.1	43.3	41.2
Rb	49.1	41.2	39.2	37.0
Cs	38.9	36.7	44.7	33.3

^a In kilocalories per mole, experimental gas phase data [V. G. Solomonik and K. S. Krasnov, *J. Phys. Chem.* **53**, 161 (1979)]. Also see Ref. 35.

by organic moieties does not alter this situation. However, for alkali halides association will not terminate until ion lattices are formed. For organometallic compounds such infinite aggregation sometimes is found but more frequently is avoided. The size of the organic substituent often is responsible.

The series of NaOR structures affords an excellent example. NaOH is believed to form a saltlike three-dimensional lattice (23*b*). NaOCH₃, in contrast, prefers sheets (56). The Na⁺O⁻ interactions form a central layer enclosed on both sides by layers of methyl groups. These essentially two-dimensional stacks then aggregate further through weak interactions of the methyl group layers. The crowding of the *tert*-butyl groups in NaO^tBu (57) inhibits the formation of such sheetlike structures. Instead, the *tert*-butyl groups envelope the ionic core and stabilize the system at a lower aggregation state.

Infinite aggregates can be placed into three groups. The first comprises three-dimensional saltlike structures. Each metal cation is surrounded by numerous anions. Examples include KCH₃ (58), RbCH₃ (59), or CsCH₃ (59). Such structures are possible only if the cations and anions have comparable sizes. The second group is essentially two dimensional. Ionic interactions form a layered "core"; alkyl or other groups extend outward on both sides. Examples include EtNa (60) and NaOCH₃ (56), which have relatively small or rodlike substituents. The third group of infinite aggregates can be considered to be one dimensional. Chains of alternating cations and anions form the basic units. Examples include allyllithium·tmeda (61), benzyllithium·Et₂O (62), C₅H₅Na·tmeda (63), or C₈H₈K₂·diglyme (39). These generally involve larger organic moieties with delocalized carbanions.

The degree of aggregation of organometallic compounds naturally depends on the size of the cation and the anion. Small cations, i.e., lithium and

sodium, tend to form small cluster cores, which are enveloped by a nonpolar environment. Ions of greater size, K^+ , Rb^+ , and Cs^+ , expand the cluster core and facilitate further interactions. Hence, for a given anion, the tendency to form ion lattices may increase from Li to Cs. Furthermore, this may also be favored by increasing coordination numbers and decreased charge localization within the aggregate core.

The situation with alkylalkali derivatives is illustrative. The volatility of lithium compounds and their solubility in hydrocarbon media have been taken erroneously to indicate covalent C—Li bonding. Ethyllithium is a low-melting solid, and pure *n*BuLi is a liquid. Instead, small Li ions on the inside and nonpolar hydrocarbon moieties on the outside of the aggregates explain the observed properties, even though ionic C^--Li^+ bonding is present. Increasing solubilities from MeLi to *n*BuLi agree with this interpretation. Both *n*BuNa and *n*BuK are insoluble in hexane and exhibit properties which have been taken to be "more ionic" in character. However, this is due to the larger size of the metal cations, which permits more extended crystal lattices to form.

Both $(CH_3Li)_4$ (64) and $(CH_3Na)_4$ (65) are tetramers in the solid. Intercluster contacts $MCH_3 \cdots M$ are present and are responsible for the high melting points and nonvolatility of these compounds. In contrast, CH_3K (58), CH_3Rb (59), and CH_3Cs (59) form infinite lattice structures in the solid. $(C_2H_5Li)_4$ is tetrameric as well (66), but its sodium analog has been characterized as a two-dimensional layered structure (60). The decreasing tendency of the higher organoalkali compounds to associate even in donor solvents is illustrated by cryoscopic and NMR data. While *n*BuLi, e.g., forms both dimers and tetramers in THF solution (67), *n*-octylsodium, *n*BuNa, and *n*BuK exist as monomers in the same solvent (68).

D. The Ligand: Solvation

With notable exceptions, the structures of organoalkali compounds have not been determined on the pure compounds. Instead, crystals are typically obtained from solution and contain solvent and/or chelating ligands. This may be an advantage, since it seems reasonable to assume that such complexes in the solid represent the species in solution to a large extent.

In effect, the ligands (including the solvent) and the carbanion compete for the cation. While solvent-separated alkali metal–carbanion ion pairs seldom are found in the solid, the ligands tend to reduce the degree of aggregation. In the known cases, however, neither the degree of aggregation nor the degree of solvation seems to influence the geometries of the carbanion moieties

significantly. Indeed, molecular orbital calculations on isolated monomers (carried out before the experimental data were available) have often *predicted* the carbanion geometries remarkably well (5). Nevertheless, solvation increases carbon-metal bond lengths by approximately 0.2 Å; this varies somewhat with the number of solvent or ligand molecules (1,5,69).

1. Energies

Solvation energies of alkali metal cations generally correlate well with the reciprocals of the ion radii (70). For illustration, enthalpies of water and ammonia interaction for gaseous alkali cations are given in Table III. For the first such solvation steps, the product of ion radius times solvation enthalpy is nearly constant for different cations within each column. For a given metal, interaction energies decrease for each additional solvent molecule. *Ab initio* data indicate (69) that cation-ligand distances (for organoalkali compounds, metal-carbon distances as well) also increase with further coordination.

TABLE III
ENTHALPIES (kcal/mol) OF SOLVATION FOR GASEOUS ALKALI CATIONS

$M^+ + n \text{Nu} \rightarrow [M(\text{Nu})_n]^+$							
Nu = H ₂ O ^a							
	(H ₂ O) ₁	(H ₂ O) ₂	(H ₂ O) ₃	(H ₂ O) ₄	(H ₂ O) ₅	(H ₂ O) ₆	Absolute ^b
Li	34	60	81	97	111	123	127.5
Na	24	44	60	74	86	97	100
K	17	33	46	58	69	79	80
Rb	16	30	42	53	63	—	73
Cs	14	26	37	48	—	—	69
Nu = NH ₃							
	(NH ₃) ₁	(NH ₃) ₂	(NH ₃) ₃	(NH ₃) ₄	(NH ₃) ₅	(NH ₃) ₆	
Li ^c	39	72	93	109	121	130	
Na ^c	29	52	69	84	95	114	
K ^d	20	36	50	63	—	—	
Rb ^d	19	34	47	68	69	—	

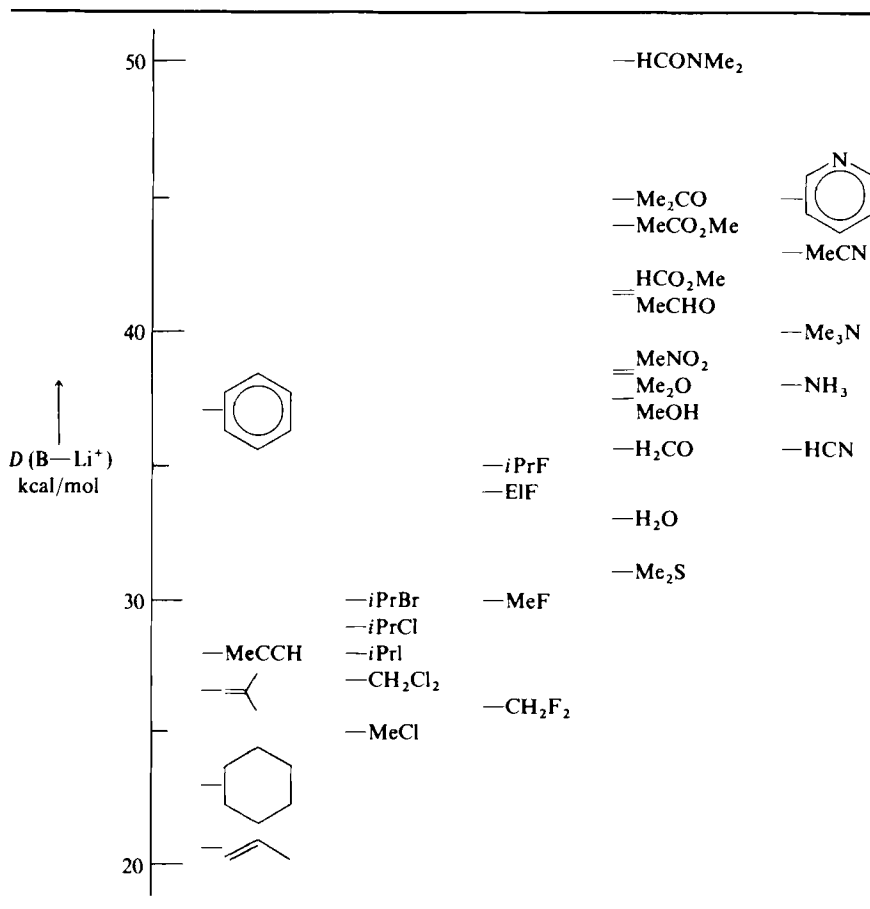
^a P. Kebarle, *Annu. Rev. Phys. Chem.* **28**, 445 (1977).

^b Estimated for infinite solvation, Ref. d.

^c A. W. Castleman, P. M. Holland, D. M. Lindsay, and K. I. Peterson, *J. Am. Chem. Soc.* **100**, 6039 (1978).

^d A. W. Castleman, *Chem. Phys. Lett.* **53**, 560 (1978).

TABLE IV
 Li^+ AFFINITIES OF SELECTED BASES IN THE GAS PHASE



Li^+ affinities of several bases correlate linearly with the corresponding Na^+ affinities; these energies are inversely related to the corresponding ion-base distances (71). Hence, Li^+ solvation energies should permit a simple prediction of solvation energies for the heavier alkali metal cations. Table IV presents some selected values of Li^+ affinities of several bases in the gas phase (72).

In the solid state ethers or amines are common ligands for the alkali cations. However, olefinic or aromatic π systems often coordinate with the metal cation as well. The induced dipole interactions between the alkali cation and the polarizable π electron density are not necessarily weak. For example, the K^+ affinities of diethyl ether (73), ammonia (74), and benzene (75) amount to

22.3, 20.1, and 19.2 kcal/mol, respectively. Consequently, olefinic moieties within the formula unit are often included into the coordination sphere of the alkali cation. Similarly, organoalkali or alkalihydride additions to olefinic systems or corresponding β -eliminations involve intermediate π complexes of considerable stability (2a). In addition, organoalkali compounds may have enhanced solubility in aromatic solvents.

2. *Heteroatoms*

Particles with opposite charges will approach one another as closely as possible. Negative charges tend to be associated with the most electronegative atoms. Hence, carbonyl-, nitro-, or cyano-stabilized carbanions exhibit structures with heteroatom-coordinated alkali cations. Similarly, electro-negative atoms of solvent molecules interact electrostatically (dipole-ion) with the alkali cations.

When more than one heteroatom and/or carbanionic site is present in a molecule, metal cations often adopt bridging positions in order to interact with multiple centers simultaneously. While the larger alkali metals can interact with more centers, the smaller lithium cation has larger binding energies and often bridges more effectively than the sodium ion, etc., e.g., in α -heterosubstituted carbanions (4a). This ability to interact with heteroatoms intramolecularly (chelation) obviously is related to the corresponding inter-molecular binding of the cation with solvents or ligands.

3. *Ion Pairing and Ion Aggregation*

Common aprotic organic media do not solvate the carbanion sufficiently. Hence, ion pairing or ion aggregation of organometallic compounds is a general feature in solution. However, solvent molecules may displace the anion from the coordination sphere of the cation. If anion nucleophilicity is greater than that of the solvent, anion-cation interaction energies cannot be overcome by solvation. For such cases, formation of solvent-separated ion pairs should be least favorable for lithium compounds. For anions which have lower nucleophilicity than the competing solvent molecules, the enhanced solvation of Li^+ will favor solvent-separated ion pairs.

As many organic compounds of the heavier alkali metals are insoluble in most organic media, comparative studies are confined to systems with delocalized carbanions. Formation of solvent-separated ion pairs is often claimed to be favored in going from Cs to Li (76). Solid-state structures do not really substantiate this picture, as solvent-separated species have only recently been observed for lithium compounds and the percentage of such cases is very small. For the heavier alkali metals more examples are known.

4. Chelating Agents

Complexation constants of different chelates depend strongly on the cation. TMEDA, for example, widely applied in lithium chemistry, readily forms lithium chelates due to less unfavorable entropy as compared with two single amine molecules. However, the inferior "bite" toward the larger potassium cation diminishes enthalpic solvation contributions. Hence, this ligand chelates larger cations less effectively or even acts as monodentate binder.

Thus, in fluorenylpotassium·tmeda (45) two different cations are connected by the ligand instead of the typical chelate structure found in lithium compounds (44). However, when, for example, aggregation energies are important as in $(\text{MeLi})_4 \cdot (\text{tmeda})_2$ (77), TMEDA may serve as monodentate ligand in lithium chemistry, too. Furthermore, if a single TMEDA ligand is attached to the larger alkali cations, some coordination sites remain unoccupied. This will lead to different structures (and aggregation states) than those found in lithium compounds, even though the stoichiometry may be the same.

5. Anion Solvation

Addition of organometallic Lewis acids to organoalkali compounds might be envisioned as anion solvation. Nevertheless, these are best considered to be a separate class of compounds. The Lewis acids, e.g., organic derivatives of main group and transition metals, in effect, bind more strongly to the carbanion and displace the alkali metal cation (Fig. 6, compare Section IV,B,2).

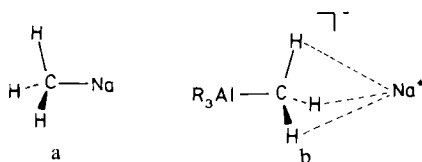


FIG. 6. Alkali metal-carbon bonding in methylsodium (a) and in sodium aluminate compounds (b).

III

BOND LENGTHS

Table VI gives a comprehensive survey of carbon-heavier alkali metal bond distances, coordination patterns, and interaction schemes in structures which have been determined by X-ray analysis and which contain

TABLE V
AVERAGE CARBON—METAL BOND LENGTHS (Å) FOR SELECTED CLASSES OF
COMPOUNDS: X-RAY^a AND THEORETICAL^b RESULTS

Class	Li	Na	K	Rb	Cs
Alkyl—M	2.28	2.62	3.22	3.36	3.53
<i>Ab initio</i>	2.01	2.34	—	—	—
Vinyl—, aryl—M	2.25	2.59	—	—	—
<i>Ab initio</i>	1.98	2.30	—	—	—
Ethynyl—M	2.16	2.52	2.71	2.98	—
<i>Ab initio</i>	1.92	2.24	—	—	—
Benzyl—M	2.29	2.65	3.02	—	—
Cyclopentadienyl—, cyclooctatetraenyl—M, and related compounds	2.33	2.81	3.06	3.14	3.29
Side-on interaction with olefinic π systems	—	2.72	3.04	3.21	—
Benzene solvent	—	3.02	3.37	—	3.76
Shortest distance observed	2.04	2.37	2.55	2.98	3.29

^a Taken from well assignable examples of Table VI; average X-ray values, irrespective of status of aggregation or solvation.

^b 6-31G*/6-31G*.

alkali-carbon interactions. The order follows the closer presentation of Section IV, grouped for each metal. Interactions in some of these compounds may be attributed to certain types of bonding: e.g., methylsodium and ethylsodium to alkylsodium bonding; sodium graphite, terphenylsodium·thf₆, C₅H₅Na·tmeda, and C₅H₄COMe·thf to bonding in compounds with π -delocalized carbanions, etc.

Average bond distances within these classes (Table V) generally increase when going from Li to Cs; they decrease when the carbanion hybridization changes from sp^3 to sp^2 to sp . Resonance-stabilized systems exhibit greater alkali-carbon bond distances. Metal-carbon separations in polyhaptocoordinated anions exceed those in benzylic organometals, where the primary contact is with the α -carbon. With uncharged benzene ligands, M—C distances are even longer by 0.2–0.4 Å. *Ab initio* calculations on monomeric systems which do not take solvent or other ligand interactions into account consistently give values smaller than experiment by 0.1–0.2 Å.

TABLE VI
ORGANOALKALI COMPOUNDS CONTAINING M—C INTERACTIONS

Formula	Range of M—C distances ^a	Coordination ^b	Hapticity ^c (η^m , m)	Ref.
Na CH ₃	2.58–2.64 (2.60); intermolecular: 2.76	4	1	65
Na C ₂ H ₅	2.63–2.68 (2.64)	4	1	60
Na C ₆ H ₅ ·pmdta	2.66, 2.68	2 + 3 _N	1	79
Na 'Bu—C=C=CMe—C≡C—'Bu·(tmeda) ₂	2.60	1 + 4 _N	1	49
Na C≡CH (at 5 K)	2.60, 2.67 (2.66)	1 + 4	1	80b
(at 298 K)	2.49–2.71 (2.67)			80c
Na C≡CCH ₃	2.37, 2.72 (2.64)	1 + 4	1, (2)	80c
Na ₂ C ₂	2.62–2.77 (2.68)	6	1	83
Na CH ₂ —Ph·tmeda	2.65	2 + 2 _N	1	85
Na C(Ph) ₃ ·tmeda	2.64–3.13	6 + 2 _N	3	20
Na CHPh—P(Ph) ₂ —CHP(Ph) ₂ ·Et ₂ O·thf	2.66, 2.82	2 + 2 _O + 1 _P	2	91
Na cp·tmeda	2.86–2.96 (2.92)	10 + 2 _N	5	63
Na (C ₅ H ₄ —COCH ₃)·thf	2.69–2.94 (2.83)	5 + 3 _O	5	96
Na ₂ (terphenyl)·thf ₆	2.78–2.86 (2.81)	6 + 3 _O	6	99
Na C ₆₄	2.66	12	6	103, 104
Na [Ni ₂ (C ₂ H ₄) ₄ H]·(tmeda) ₂	2.82, 3.14	2 + 4 _N	2	114
[Na(OEt ₂) ₂] ₂ [Nb ₂ H ₂ (η ⁵ -C ₅ H ₄ SiMe ₂ OSiMe ₂ -η ⁵ :η ¹ -C ₅ H ₃) ₂]	2.59–3.02	3 + 2 _O	1, 2	117
Na ₄ [Ph ₂ Ni(C ₂ H ₄) ₂ ·(thf) ₅]	2.57–3.02	2 + 1 _O + 2 _{Ni}	1	119
		2 + 2 _O + 1 _{Ni}	1	
		4 + 1 _O + 1 _{Ni}	1, 2	
Na ₂ CrPh ₅ ·(Et ₂ O) ₃ ·thf	2.64–2.95	5 + 2 _O	1, 2	120
[Na ₂ Ph(Et ₂ O) ₂ (Ph ₂ Ni) ₂ N ₂ NaLi ₆ (OEt ₂) ₂]	2.48–2.95	4 + 1 _O + 1 _{Ni}	1, 2	121
Na Eu[N(SiMe ₃) ₂] ₃	2.70–3.21	8 + 2 _N	1	123
Na Y[N(SiMe ₃) ₂] ₃	2.90–3.11	8 + 2 _N	1	123
Na ₂ [(SiMe ₃ N) ₂ SiMe ₂]	2.69–3.25	3 + 3 _N	1	128
	2.66–3.04	4 + 2 _N	1	
Na [InMe ₄]	2.73	4	1	137
Na [InPh ₄]	2.75, 2.80	4 + 4	1, (2)	144

(continued)

TABLE VI (continued)

Formula	Range of M—C distances ^a	Coordination ^b	Hapticity ^c (η^m , m)	Ref.
[Na(thf) ₂][AlMe ₂ (C ₁₀ H ₈) ₂]	2.87, 2.91; aromatic: 2.89–2.96 (2.91)	2 _O + 2 + 6	2, 6 6	147
[Na(thf) ₂][AlMe ₂ (C ₁₄ H ₁₀) ₂]	2.94–3.32 (3.08)	8 + 2 _O	6	148
Na [Al(SiMe ₃) ₄]	2.40–3.01 (2.71)	4	1	151
Na [Al(SiMe ₃) ₄]·(C ₆ H ₅ —Me) ₂	2.68, 2.70; aromatic: (3.08)	2 + 12	1,6	151
Na [Al ₂ Me ₆ H]	2.91	6	1	131
Na [BMe ₃ H]·(Et ₂ O) _{0.25}	2.56–2.73	Multi., 3 _H	1	153
Zeolithe 4A·(C ₂ H ₂) ₆	2.57–3.04 (2.70)	—	2	182
Na-A-Zeolithe·(C ₂ H ₂) ₃	2.15–3.18 (2.72)	—	2	184
Y-Zeolithe·(C ₆ H ₆) _x (x = 1.1)	3.04	—	6	185
(x = 2.6)	2.99	—	6	
Na-A-Zeolithe·(CH ₄) _x	2.67, 2.94–3.84	—	1	184
Na [Co(CO) ₄]	3.00–3.26	—	—	248
Na ₂ [Fe(CO) ₄]·(dioxane) _{1.5}	2.86, 3.05	—	—	249
Na C ₇ H ₅ O ₂	3.07	—	—	323
K CH ₃	3.22	6	1	58
K C≡CH	2.87, 3.04 (3.01)	1 + 4 (+4)	1, (2)	80c
K C≡CCH ₃	2.55, 3.04 (2.95)	1 + 4 (+4)	1, (2)	80c
K (CHPh) ₂ P(Ph) ₂	2.96–3.35 (3.15)	10	3, (2, 1)	92
K (2-C ₅ H ₄ N ₁)CH—P(Ph) ₂ —CHP(Ph) ₂ ·(thf) ₂	3.02	1 + 2 _O + 2 _N	3 (1-azaallyl)	93
K (fluorenyl)·tmeda	3.04–3.35 (3.32)	10 + 2 _N	5	45
K ₂ cot·diglyme	2.98, 3.31–3.36 (3.05)	2 + 8 8 + 3 _O	1, 8 8	40
K ₂ (cot-Me ₄)·(diglyme) ₂	(3.00)	8 + 3 _O	8	42
K C ₈ ^d	3.05	12	6	103
K(diglyme) [Ce(cot) ₂]	3.06–3.24 (3.16)	8 + 3 _O	8	105
[K(dme)] ₂ [Yb(cot) ₂]	(3.02)	8 + 2 _O	8	108
K ₂ [(Ph ₃ P) ₂ (Ph ₂ PC ₆ H ₄)RuH ₂] ₂ ·C ₁₀ H ₈ ·Et ₂ O	2.97–3.61	12 (+ 1 _H), 12 (+ 2 _H)	6	109

K [OsH ₃ (PMe ₂ Ph) ₃]	3.12–3.60	12 + 4 _H	6	110
K [Co(C ₂ H ₄)(PMe ₃) ₂] ₂	3.03–3.24 (3.11)	6	2	111
K [AlMe ₄]	3.14, 3.48	8	1	136
K [GaMe ₄]	2.94, 3.52	8	1	136
K [InMe ₄]	3.16, 3.47	8	1	138
K [In(CH ₂ SiMe ₃) ₄]	3.13–3.29 (3.23)	6	1	139
K [ZnMe ₃]	3.10–3.28 (3.17)	6	1	135, 140
K [BPh ₄]	3.19	4	1	141
K ₂ [Zn(CCH) ₄]	3.1–3.5	6	2, 1	146
K ₂ [Cd(CCH) ₄]	2.8–3.8	6	2, 1	146
K [Al(C ₈ H ₁₂) ₂]	2.95–3.43 (3.14)	10	3, 2	149
K [AlHMe ₃]	3.47	2 _H + 1	1	152
K [Al ₂ Me ₆ (SeMe)]·(C ₆ H ₆) ₂	3.15–3.22 (3.19)	6	1	158
K [Al ₂ Me ₆ F]·C ₆ H ₆	3.33–3.49 (3.41)	2 + 24	1, 6	
K [Al ₂ Et ₆ F]	3.23–3.47; aromatic: (3.30)	1, 6	1	159
[K(db-18-c-6)][Al ₂ Me ₆ Cl]·(C ₆ H ₆) ₂	3.28	1	1	160
K [Al ₂ Me ₆ N ₃]	(3.39)	6 _O + 6	6	161
	3.15–3.31 (3.23)	2 _N + 4	1	163
	3.09–3.24 (3.16)	6	1	
K [AlMe ₃ CN]	3.24–3.65	3 _N + 4	1	167
K [Al ₂ Me ₆ SCN]	3.15–3.26 (3.21)	1 _S + 5	1	168
[K(db-18-c-6)][GaMe ₃ NCS]·(C ₆ H ₆) _{2.5}	3.48–3.72 (3.59)	Not reported	6	8
K [Al ₂ Me ₆ NO ₃]	3.18–3.44 (3.34)	3 _O + 5	1	172
	3.11–3.44 (3.24)	2 _O + 5	1	
K [AlMe ₃ NO ₃]·C ₆ H ₆	3.27, 3.28; aromatic: (3.38)	4 _O + 8	1, 6	172
K [Al ₄ Me ₁₂ SO ₄]	3.11–3.64 (3.32)	5	1	174
	3.19–3.38 (3.30)	2 _O + 4	1	
K [Al ₄ Me ₁₂ SO ₄]·(p-Me ₂ -C ₆ H ₄) _{0.5}	3.11–3.58; aromatic: (3.42)	8	1, 3	174
	3.24–3.49 (3.42)	2 _O + 5	1	
K [Al ₇ O ₆ Me ₁₆]·C ₆ H ₆	3.14–3.37, aromatic: (3.33)	11	1, 6	157
K [AlCl ₃ Me]	3.21	4 _{Cl} + 1	1	178
K [Ph ₂ NN—C ₆ H ₃ (NO ₂) ₃]	3.21, 3.28	2 + 7 _O + 1 _N	2	186
K [Co(CO) ₄]	3.41–3.93		—	265
K ₂ [Fe(CO) ₄]	3.28, 3.40	4 + 8 _O	—	252

(continued)

TABLE VI (continued)

Formula	Range of M—C distances ^a	Coordination ^b	Hapticity ^c (η^m , m)	Ref.
Rb C ₈ ^d	3.36	6	1	59
Rb C≡CH	2.98–3.21 (3.16)	1 + 4 (+4)	1, (2)	80c
Rb ₂ cot·diglyme	3.37, 3.43; COT: (3.10)	8 + 2	8	41
	(3.15)	8 + 3 _O	8	
Rb C ₈	3.16	12	6	103
Rb [AlMe ₄]	3.16, 3.44	8	1	136
Rb [GaMe ₄]	3.16, 3.60	8	1	136
Rb [BPh ₄]	3.39, 3.46, 3.55	8	1, 2	142
Rb [AlMe ₃ N ₃]	3.44, 3.53	2 + 3 _N	1	164
Rb [Ga ₂ Me ₆ (CH ₃ COO)]	3.38–3.54 (3.47)	3 _O + 4	1	171
Rb CH(SO ₂ CF ₃)	3.62	7 _O + 1	1	224
Rb [Co(CO) ₄]	3.36–3.87	Long range	—	265
Cs CH ₃	3.53	6	1	59
Cs C ₈ ^d	3.29	12	6	103
Cs [InMe ₄]	3.47	4	1	138
Cs [AlMe ₄]	3.29, 3.73	8	1	136
Cs [AlMe ₂ I ₂]·C ₆ H ₄ Me ₂	(3.84)	4 _I + 12	6	162
Cs [AlMe ₃ N ₃]	3.72	4 _N + 2	1	165
Cs [Al ₃ Me ₆ N ₄]·(p-Me-C ₆ H ₄) ₂	aromatic: (3.64)	12	6	166
Cs [AlMe ₃ (NCS)]	3.39, 3.52 – 3.72	1 _s + 1 _N + 4	1	169
Cs [Al ₇ O ₆ Me ₁₆]·(Me-C ₆ H ₅) ₃	aromatic: (3.80)	3 + 18	1, 6	8
Cs [Co(CO) ₄]	3.74 – 3.84	Long range	—	267

^a Metal–carbon bond distances in angstroms; figures in parentheses denote average values.

^b Alkali metal coordination. Unless indicated by atomic symbols, carbon contacts are implied. Thus 2 + 2_N means coordination to two carbon and two nitrogen atoms.

^c Hapticity of the bonding of the carbon ligand(s) to the alkali metal.

^d Calculated from carbon-carbon bond distance (1.42 Å) and layer spacings (K: 5.41 Å; Rb: 5.61 Å; Cs: 5.95 Å) in alkali graphite compounds (103).

IV

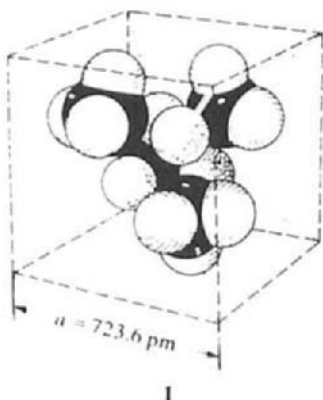
SYSTEMS CONTAINING CARBON-METAL INTERACTIONS

A. Simple Organoalkali Compounds

1. Compounds Obtained by Metal-Hydrogen Exchange

a. *Alkyl Compounds.* Only five structures of alkyl derivatives of the higher alkali metals have been reported: The complete set of methyl species, CH_3Na through CH_3Cs , and ethylsodium. None of these have additional coordinating ligands.

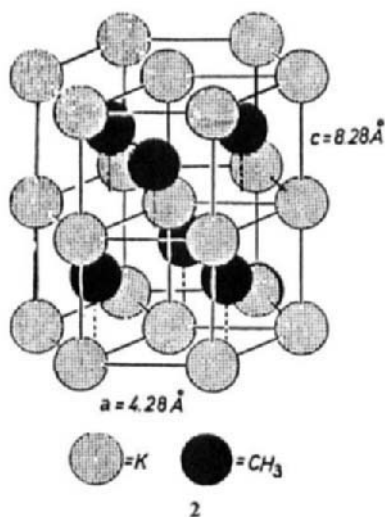
Methylsodium (**1**) (65) adopts a tetrameric structure resembling that of methyllithium (64). Due to the larger Na atoms, however, the size of the cubelike cluster is increased compared to the lithium case. Hence, more pronounced interactions with molecules in the environment can occur. Insolubility in hydrocarbon solvents is the most obvious consequence. Furthermore, interactions between tetrameric clusters result in certain orientations of the multipoles. Thus, the unit cell of methylsodium contains interstices, in which methyllithium tetramers can be incorporated. A compound with a Na:Li ratio of 3:1 has been structurally characterized (65).



In contrast, methylpotassium (**2**) (58) crystallizes in a hexagonal NiAs-type structure, which is built up by isolated methyl anions and potassium cations. The same general structures were found for methylrubidium (59) and methylcesium (59), but with greater lattice constants. The large alkali atoms result in opened arrangements in order to attain a higher (slightly distorted

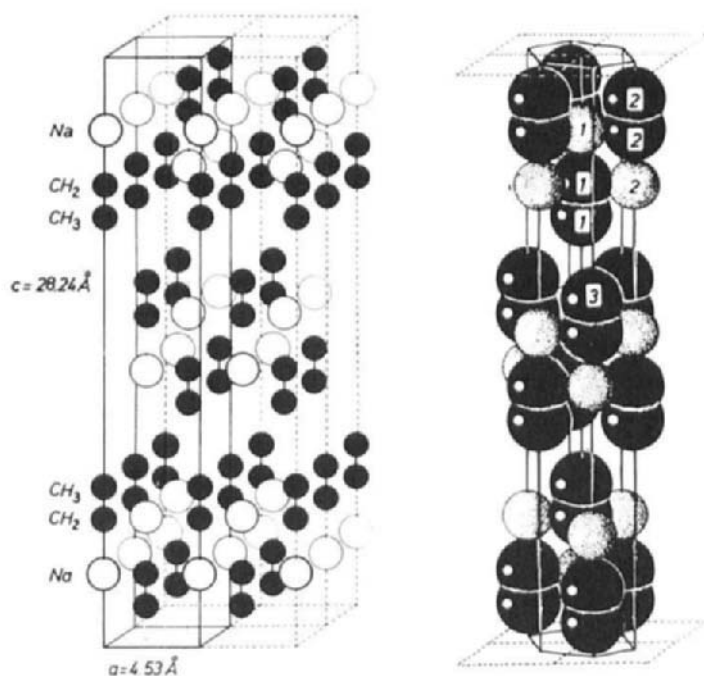
octahedral) coordination. Even though the changes in crystal structures along the series Li to Cs formerly provided arguments for increased ionicity, these changes can be understood on the basis of size effects (ion radii) alone.

Hydrogen positions could not be obtained in these studies; this may be due to structural or thermal disorder. The NiAs-like arrangements allow the anions to invert or, in the extreme, possibly to become planar. If the methyl group is replaced by the larger silyl group, the less densely packed NaCl-type structure is formed (78).

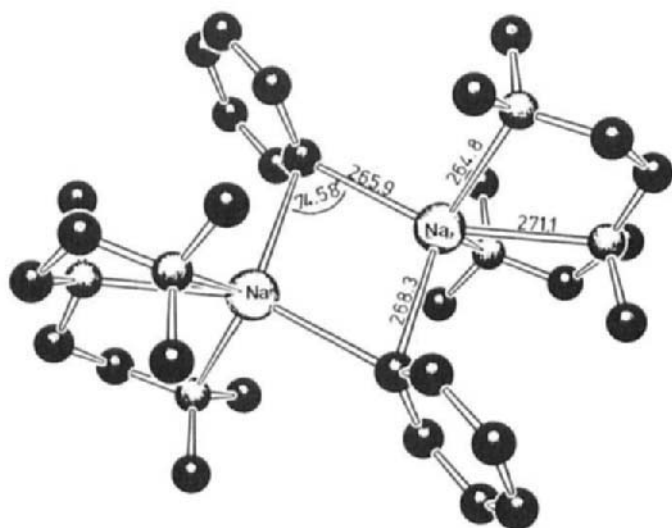


Ethylsodium (**3**) (60) adopts double layers in the solid. C_2H_5Na units are oriented alternatively perpendicular to the sheet; the ionic centers are packed close together inside the layers. In spite of this infinite ionic lattice, the fourfold coordination of the sodium ions still resembles the lithium environment in tetrameric ethyllithium (66). Indeed, the whole arrangement may be rationalized as distorted cubane units linked in two dimensions. This structure represents a transition from aggregated lithium compounds to ionic lattices of the higher alkali metals, as another modification of crystals has been found (60), which probably correspond to a tetrameric specimen. Thus, depending on counteranion size, donating ligands, or conditions of synthesis or crystallization, organosodium compounds can crystallize either in oligomeric or in ion lattice types.

b. Aryl, Alkenyl Compounds. The structure of phenylsodium·pmdta (**4**) (79) is isostructural to phenyllithium·tmeda (52) in all its essentials; a phenyl



3

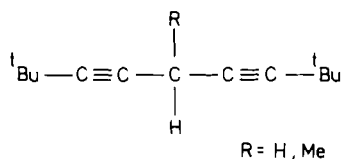


4

group bridges two sodium sites in the dimeric unit. Similar geometries are found in a number of mixed metal phenyl compounds, but the organic moiety is unsymmetrically placed.

The use of a tridentate cosolvent illustrates the coordination number dependence of these aggregates: For $\text{PhLi} \cdot \text{Et}_2\text{O}$ (51) three coordination sites remain unaffected, hence a tetramer forms. If the solvent is exchanged by a bidentate ligand, dimers result, e.g., in $\text{PhLi} \cdot \text{tmeda}$ (52). The tridentate chelate in $\text{PhLi} \cdot \text{pmdta}$ (53) favors monomers. The bigger sodium cation allows additional coordination and $\text{PhNa} \cdot \text{pmdta}$ is a dimer. Hence, $\text{PhNa} \cdot \text{tmeda}$ might be tetrameric, but this has not been investigated.

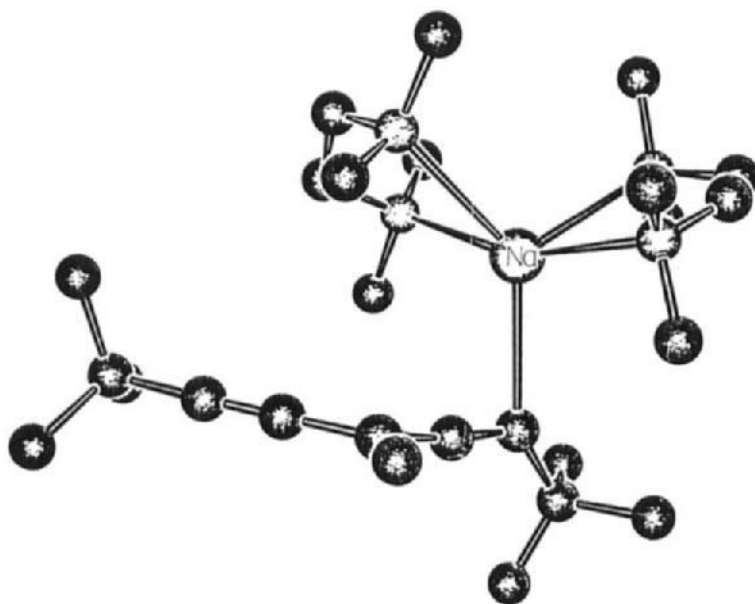
For lithiated 5-substituted 2,2,8,8-tetramethyl-3,6-nonadiyne compounds several structures have been determined. Both hydrogen and methyl-substituted systems are dimers with additional solvent molecules and adopt bent allenyl structures with bridging lithium sites (1,5,48). The sodium compound **5** ($\text{R} = \text{Me}$, $[\text{tmeda}]_2$) still maintains these essential features (49).



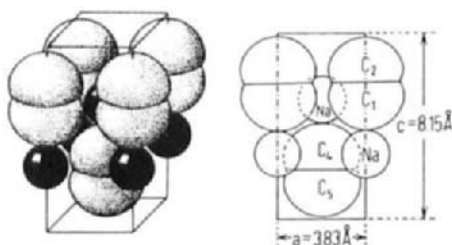
As discussed above, the bridging situation is less developed. Similarly, the bending of the carbon skeleton approaches linearity ($\Delta \text{CCC} = 172.90^\circ$). Two TMEDA molecules surround the fivefold coordinated sodium sites and prevent further aggregation. This compound should therefore be classified as an end-on metalated allenyl instead of a resonance-stabilized propargylic system. The structure is stabilized by the terminal charge localization due to the counteraction influence, not by resonance which involves the whole carbanion moiety.

c. Alkynyl Compounds. All compounds of the alkynyl type possess layered or three-dimensional structures. In contrast to lithium derivatives, no lower aggregation is observed. This might, however, be partly due to the absence of solvating co-ligands.

Monosodium acetylide (**6**) (80) forms the prototype for all other mono-metalated acetylenes [$\text{KC} \equiv \text{CH}$ (80a,c), $\text{RbC} \equiv \text{CH}$ (80a,c), $\text{NaC} \equiv \text{CCH}_3$ (80c), and $\text{KC} \equiv \text{CCH}_3$ (80c)]. Similar to ethylsodium, the structure in the crystal consists of sequential stacking of $\text{Na}-\text{C}$ -bound double layers. These sheets are connected by $\text{H}-\text{H}$ van der Waals interactions. The coordination of the alkali ion is fivefold. However, each sodium is about 0.2 Å closer to one than to the corresponding four acetylene carbons of neighboring $\text{NaC} \equiv \text{CH}$ units.



5



6

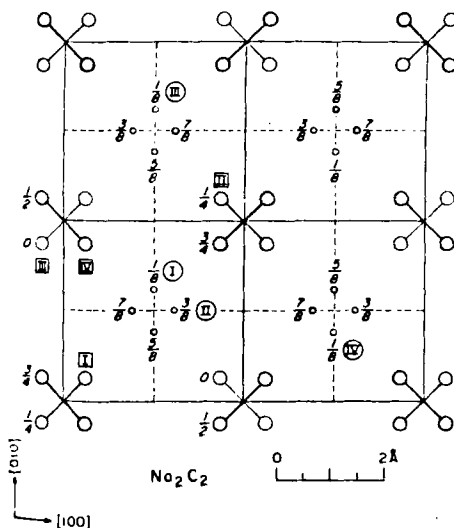
Interestingly, with greater ion size the alkali cations and acetylene layers penetrate each other more and more. For potassium and rubidium, elaborate interactions with the neighboring β -carbon atoms are present. This corresponds to η^2 -solvation of these cations by the alkynyl π -electron density and again implies higher coordination numbers.

Some comparisons may be made. For $(\text{LiC}\equiv\text{C}'\text{Bu})_n(\text{thf})_m$ two modifications have been observed: A tetrameric cluster ($n, m = 4$) and a linear dodecamer ($n = 12, m = 4$) (54,55). The dodecamer may be envisioned as a linear aggregate of three tetrameric units (Fig. 5, page 179). This arrangement is intermediate between the cubic tetramers often observed for lithium alkynyls (1) and the layered structures of the heavier alkali alkynyls. The

framework topologies of the latter may also be constructed by juxtaposition of tetrameric units; however, the aggregation proceeds *ad infinitum* in two dimensions. For lithium compounds, solvation and the smaller size of the cation favor lower aggregation states. Potassium methoxide (81) exhibits the same layered structure; ethylsodium (60) has been described as related modification (with trigonal instead of square arrangement of neighboring carbon atoms around sodium).

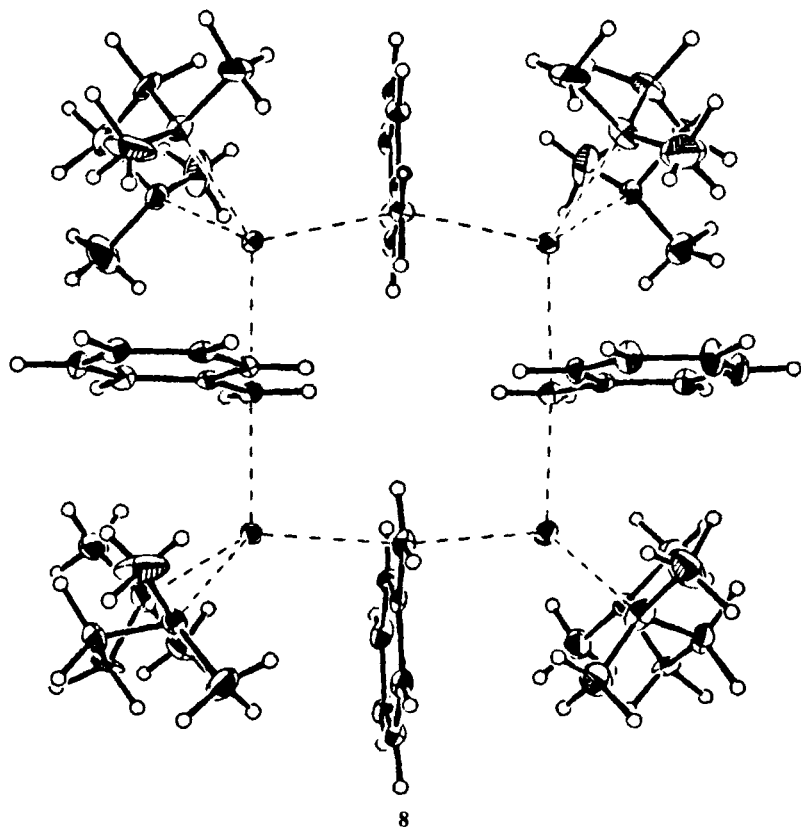
A similar π -electron solvation by neighboring acetylene units was found in organocuprates as well (82). There is much evidence that differences between group 1 and group 11 metals are not of principal but rather gradual manner.

A characteristic carbide, disodium acetylide Na_2C_2 (7) (80a,83) crystallizes in a classical ion lattice. The distorted anti- CaF_2 type packing establishes a nearly octahedral coordination for the sodium cations. The same structural type is chosen by K_2C_2 (80a) and by Li_2C_2 as well (84).



Projection of the unit cell of 7 along the c axis. Small circles represent sodium atoms, large circles carbon sites.

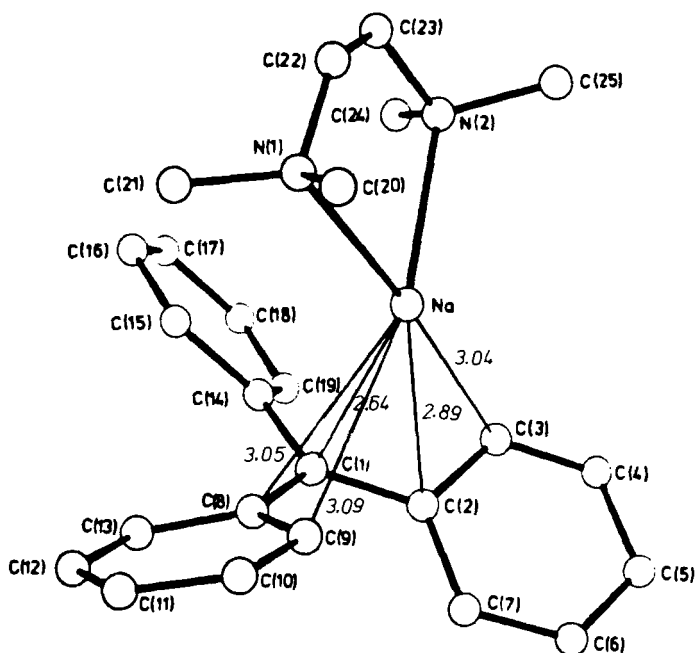
d. Benzylic Metalations. Benzylsodium•tmeda (8) forms a cyclic tetramer (85). A similar modification was calculated for $[\text{CH}_3\text{Li}]_4$ to be only 12.4 kcal/mol higher in energy than the cubic arrangement, thus perhaps representing an intermediate for intercluster stereomutation (86). In our case the planar benzyl moiety might prefer the ring structure due to charge delocalization. Some lithium amides like $\text{LiN}(\text{SiMe}_3)_2$ (1,87) and lithium cuprates like $\text{Li}_2\text{Cu}_2\text{Me}_4$ (88) as well as several organocuprates (82) also



8

form planar rings. Each α -benzyl carbon is pentacoordinate and possesses a trigonal bipyramidal geometry. Calculations suggested this S_E2 intermediate-related D_{3h} arrangement to be electrostatically favored (3 kcal/mol, MP4/6-31G**/6-31G*, CH_3Na_2^+) over a multicenter bonded C_s structure, found for CH_5^+ (85,89). The same carbon D_{3h} coordination is adopted by chain polymeric form of benzyl lithium $\cdot \text{Et}_2\text{O}$ (monodentate solvent!) (62). When benzyl lithium interacts with two solvent molecules, η^3 -allylic monomers are formed [e.g., benzyl lithium $\cdot \text{dabco}$ (90)].

Triphenylmethylsodium $\cdot \text{tmeda}$ (9) (20), markedly resembles the analogous lithium compound (21). The sodium ion is not centered directly above the central carbon atom of the triphenylmethyl group, but prefers instead closer contacts to two of the phenyl groups of the trityl anion. These interactions, to some extent, are similar to those in benzyl lithium $\cdot \text{dabco}$ (90). The third phenyl group connects two subunits in the crystal structure by coordination with a neighboring sodium ion at the para position. (Perhaps as a consequence, the

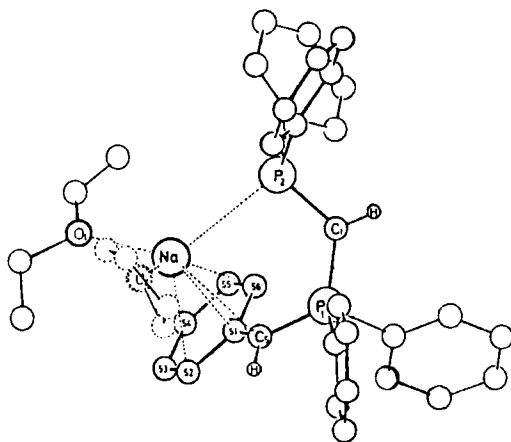


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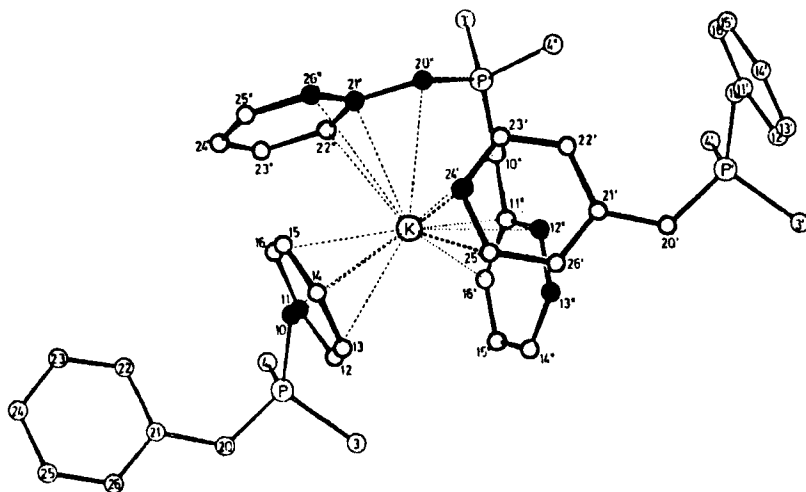
TMEDA donor is pushed to the side.) As discussed above, the geometry of the sodium derivative approaches that of the free anion more closely than that of $\text{Ph}_3\text{CLi} \cdot \text{tmeda}$ (21) does.

Three additional structures involve metal-benzyl systems substituted by ylides in α positions. In the sodium [diphenylphosphonium(benzylide)-(diphenylphosphinomethylide)](Et_2O)(thf) ion pair (10) (91) the metal cation binds mainly with α and ipso positions of the benzyl anion subunit and with a phosphorus atom. As ortho carbon sites of the phenyl moiety participate in sodium coordination, asymmetric η^3 -allylic bridging is observed. However, this type of bonding is less pronounced than that in analogous lithium cases. Further intramolecular solvation of the metal ion is provided by the phosphorus lone pair of the diphenyl phosphino group; the ylid carbon is excluded from the interaction sphere. Two additional ether molecules complete the coordination sphere.

The cation in potassium [diphenylphosphoniumbis(benzylide)], (11) (92) is encapsulated by the ylide anion. While this chelation in principle could be symmetrical, the cation interacts quite differently with both sides of the anion. The potassium coordination mainly involves ipso and ortho positions of phenyl rings and the para and another benzylic position of two of neighboring



10

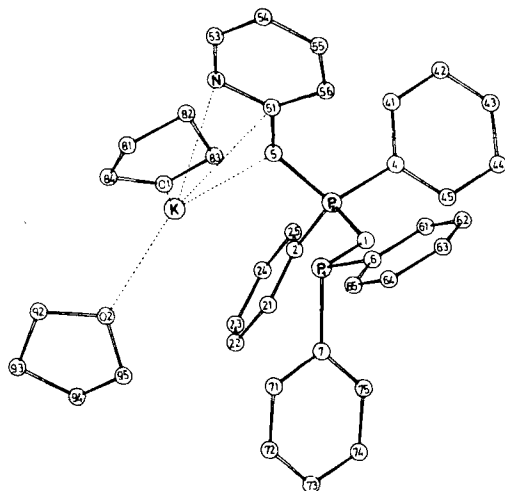


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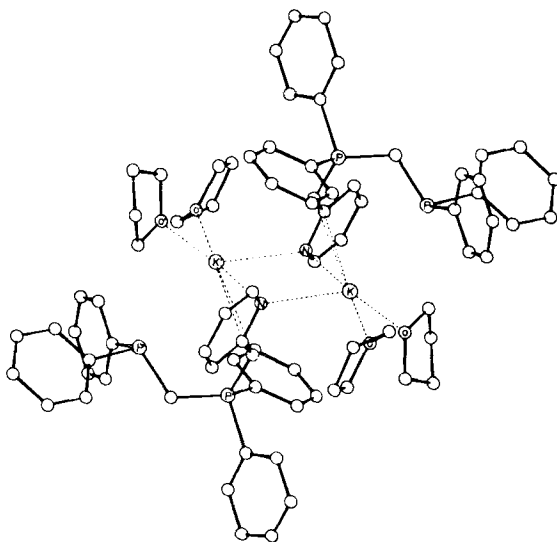
units, but several other carbon–potassium contacts are still in the range up to 4 Å. η^3 -Type interactions within the benzylic moieties are even less developed as in the sodium compound above. Instead of interacting with few centers of high charge density, the bigger potassium ion again seems to prefer multiple coordination with many carbon atoms. The ion pair character of **10** is changed into a three-dimensional network arrangement. In etheral solvents, NMR results still show the chelating ylid anion environment (92).

On substitution of the phenyl entity in **10** by a 2-substituted pyridine unit, the resulting dimer $[K(thf)_2][(2-C_5H_4N)CH-PPh_2-CH-PPh_2]$ (**12**) (93) has an asymmetric η^3 potassium location above benzylic and nitrogen sites of

the ortho-metalated heterocycle. The more favorable in-plane coordination of potassium with the nitrogen lone pair would, however, result in twisting of the group α to the phenyl ring. This would reduce or eliminate benzyl-type resonance. Instead, the nitrogen site of a neighboring anion unit provides such contacts, and dimerization occurs.



Monomeric unit in **12**

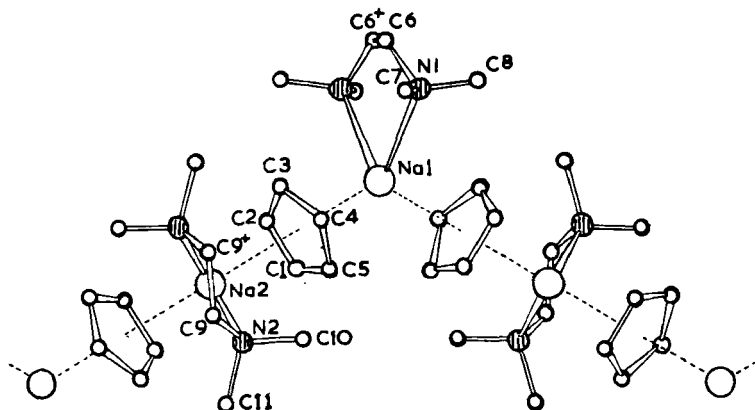


Dimers of **12**

A quite similar eight-membered ring formation has been observed for dimeric $[\text{Li}(\text{tmeda})][\text{CH}_2-(2-\text{C}_5\text{H}_4\text{N})]$ (94). However, the smaller lithium cannot benefit from intramolecular $\eta^3\text{-C,N}$ bridging and only coordinates to the benzylic carbon of a monomeric subunit.

e. Cyclopentadiene Derivatives. In cyclopentadienyllithium compounds the metal is anticipated to be centrally located over the π face of the aromatic anion, both from electrostatic and orbital interaction considerations. Indeed, most structures show this positioning, which is expected for the other alkali metals as well (95).

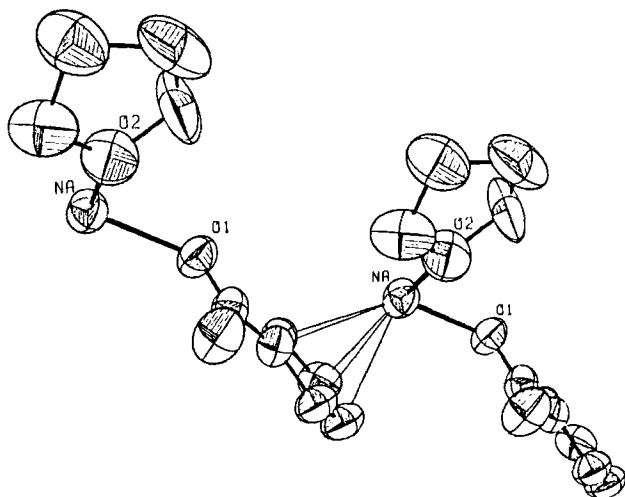
For cyclopentadienyl sodium·L, where L is a Lewis base, NMR and IR studies are consistent with η^5 -coordination of the cyclopentadienyl group (63). This π complex character is demonstrated by the solid-state structure (13) as well (L = tmeda) (63). Only small deviations from the central location are found for the sodium ions. Yet instead of isolated contact ion pairs, which are observed in solution and quite common for the lithium compounds (1,95), a puckered chain structure is formed. Again the tendency of the larger alkali ions to have higher coordination seems to afford reasonable explanation for this difference. The X-ray structure illustrates another point: The small N—Na—N angle (72°) indicates a rather unfavorable “bite” of the TMEDA ligand. This smaller coordinative ability of TMEDA toward the higher alkali ions might lead—in combination with greater coordination numbers—to structures different from the lithium analogs.



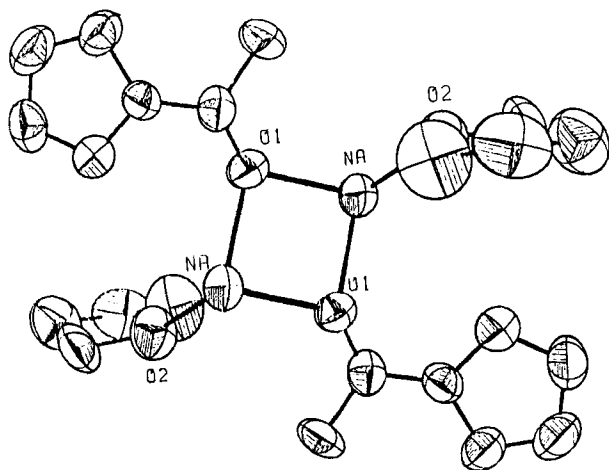
13

A related compound, acetylcyclopentadienylsodium-thf (14) (96), which could be envisioned as an enolate system as well, also shows η^5 -bonding. Pseudotetrahedral coordination of the sodium cation furthermore involves one THF molecule and two oxygen atoms from the carbonyl group of

neighboring units. This system can be considered to be a contact ion pair with respect to the cyclopentadienyl derivative, but a dimeric aggregate with respect to the carbonyl group. The polymeric situation results from association through the carbonyl linkages. The threefold heterocoordination of the sodium ion seems to be sufficient to prevent the bis- η^5 -coordination found in **13**.

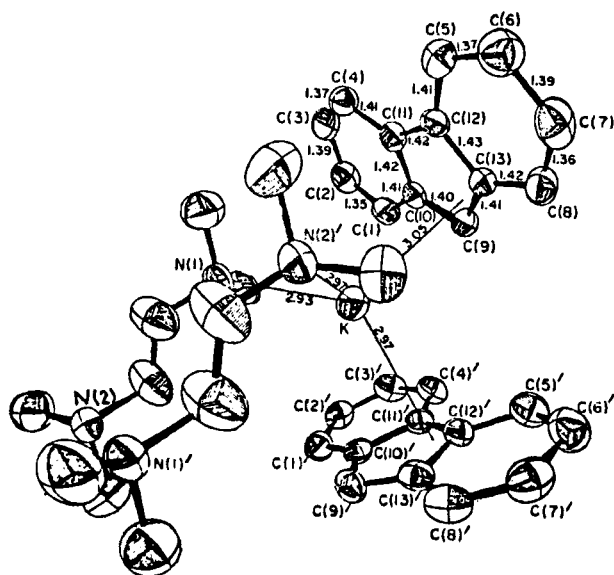


η^5 -Bonding of the cyclopentadienyl moiety in **14** and carbonyl linkages within the dimeric units.



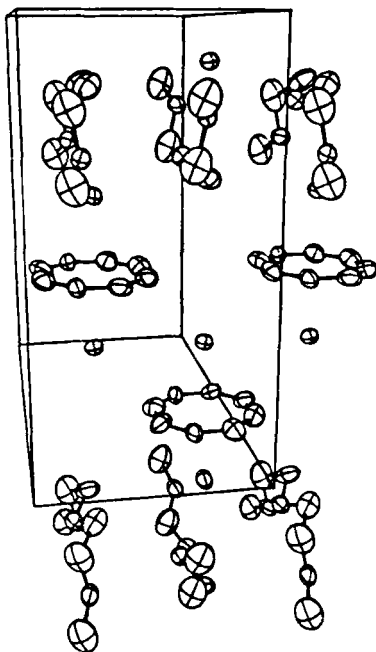
Dimeric units in the structure of **14**.

In fluorenylpotassium-tmeda (**15**) (45), each potassium ion interacts with two fluorenyl systems in an approximate η^5 manner, forming chains very similar to those of **13**. Fluorenyllithium-bisquinuclidine (**44**), in contrast, prefers an η^3 -benzylic arrangement, where only two centers (those of highest charge density) coordinate with the lithium cation. Instead of chelating the potassium ion, however, TMEDA connects different chains by bridging two potassium sites. This probably is due to the inferior "bite" of the amine toward the larger ion. As with many other structures, **15** does not crystallize with additional donating ligands. Perhaps this would result in solvent-separated ion pairs, but this situation is hardly ever displayed by such compounds, at least in the solid.



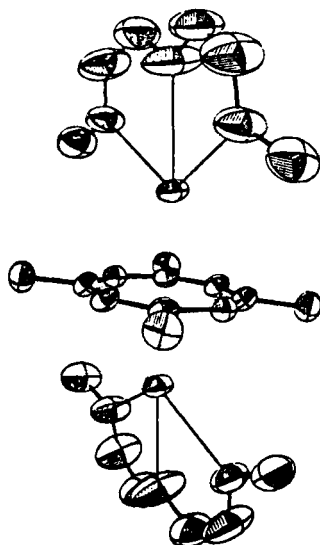
indicated by NMR studies. Indeed, all dialkali COT compounds show the expected geometry.

In dipotassium cyclooctatetraenide-diglyme (40) the potassium ions are located above and below the planar hydrocarbon system. This contact ion pair arrangement is favored both electrostatically and sterically. Whereas one cation is solvated additionally by the three oxygen atoms of a diglyme molecule, the other cation completes its coordination sphere by contacting two neighboring COT units in addition. Thus a zig zag chain of COT molecules forms, with "naked" potassium ions inside and solvated ions outside. The carbon-metal distances are only slightly longer for the polyether complexed cations. The isomorphy of the rubidium salt (16) (41) provides further evidence for the similar structures of K, Rb, and Cs organic compounds.



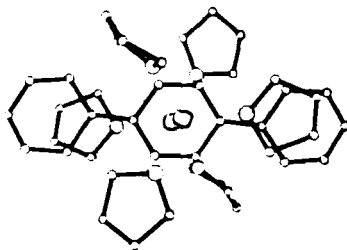
16

The complicated one-dimensional arrangements in these $\text{COT}^{2-} \cdot 2\text{M}^+$ structures are converted to simpler contact ion pairs when further coordinating ligands are present in the crystal. Thus, in bis(potassium diglyme)-1,3,5,7-tetramethyl-cyclooctatetraenide (17) (42) the COT ring is symmetrically η^8 -coordinated by two diglyme-solvated potassium ions. In spite of this solvation almost the same metal-carbon bond distances are observed as in $\text{K}_2\text{COT} \cdot \text{diglyme}$.



17

b. Polyphenyl Radical Anions and Dianions (8). Sodium terphenyl (99) provides examples for both types of radical anion and dianion structures. The dianion (**18**) is a contact ion pair structure with the two cations located above and below the planar hydrocarbon ring system. Each sodium atom, in addition, is solvated by three THF molecules. Simple Hückel calculations predict an extra charge density of about 0.9 electrons for the central ring of the dianion; both cations are associated with this ring. Hence, the arrangement can be rationalized again by ionic interpretations, which have also been applied to related lithium compounds (46a).



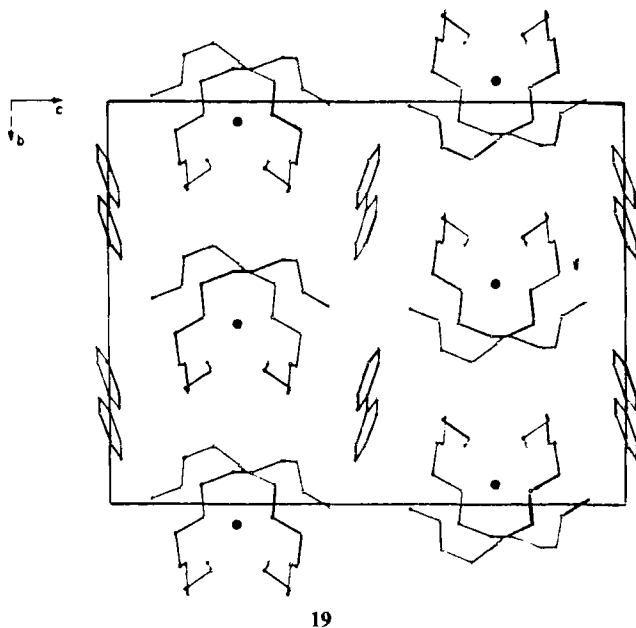
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With dimethoxyethane as the ligand, the monoanion has a solvent-separated structure with the composition $\text{Na}_2(\text{terphenyl})_3 \cdot \text{dme}_6$ (99). Sodium is nearly octahedrally coordinated by three DME molecules. The unit cell contains two almost planar terphenyl radical anions, separated by a neutral

terphenyl molecule. These arrays form one-dimensional stacks, with the solvated sodium ions packed in between.

Quite generally solvent-separated ion pairs are observed only with chelating agents or crown ethers. When many strong alkali-heteroatom interactions are present, the metal is shielded and no carbon-metal contacts can form. Monoanions are needed as well; in dianions coulombic interactions with the cations obviously are too strong to be overcome by solvation. Alkali-cation/monoanion interactions also are weak in π -delocalized anions or complexed species like $[\text{AlR}_4]^-$. Increased coordination numbers and smaller carbon-metal bond energies of the heavier alkali cations will favor solvent-separated structures for these as well.

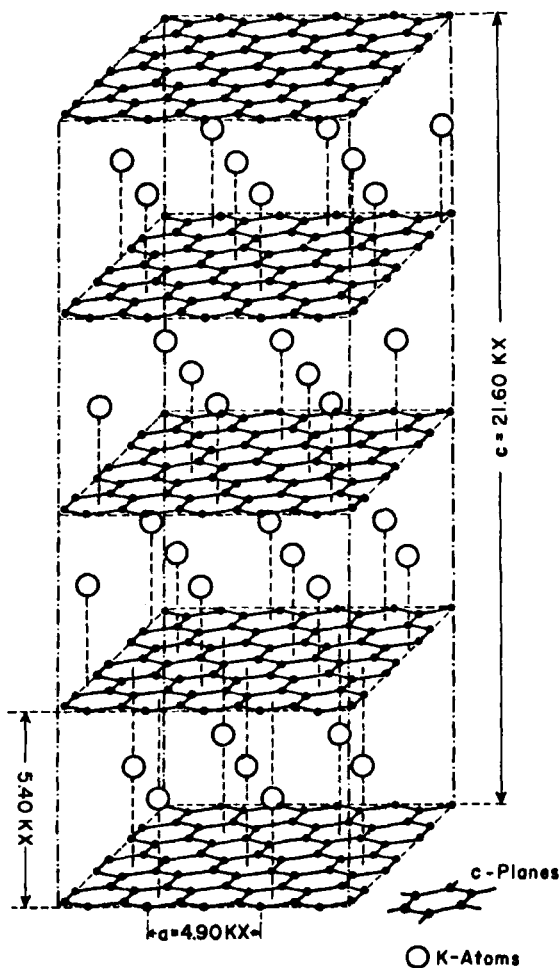
In the biphenyl radical anion system, the sodium (100), potassium (19) (101), and rubidium (102) structures were determined; the cations are enclosed by two tetraglyme molecules in all cases. Due to different cation diameters slightly different coordination polyhedra are formed by the solvent molecules. This, in turn, leads to a somewhat different packing of the subunits in the crystal lattice.



c. Alkali-Graphite Intercalates (103). Alkali-graphite intercalates represent examples of delocalized polyanions. The parent compounds, MC_8 ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$) (20) (103), involve alternating layers of alkali atoms be-

tween graphite planes; the alkali ions are η^6 -located above the carbon hexagons. Carbon-metal bond distances are in the same range as in related structures with π -delocalized carbanions and are approximately 0.3 Å shorter than for interactions of benzene molecules with the same cations (compare Table V). Interchange of alkali sites in the graphite intercalates is possible; this indicates the energy surfaces to be smooth.

A variety of intercalate structures can be deduced from this prototype when different populations within the alkali layers are involved; vacant layers, alternate sequences of layers, or substitution of alkali sites, leading to ternary compounds, provide further variations. Most systems are capable of including



additional solvent molecules like NH_3 , THF, or benzene; these structures have not been determined experimentally.

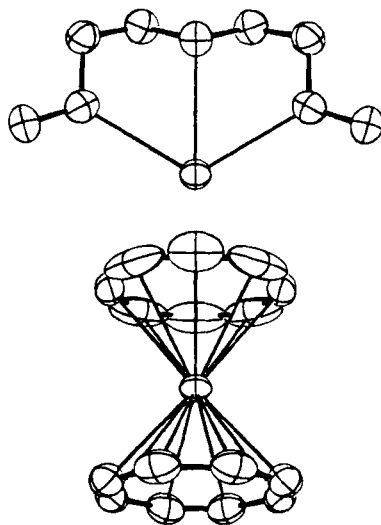
Sodium and especially lithium only form such solids reluctantly; for Na but one compound, NaC_{64} (103c,104), has been characterized, and none for Li. The relative stabilities reflect both the trends in ionization potentials and the ratio between the metal cation and ring size [compare Section II,B,3, Ref. (39)].

B. Mixed Metal Compounds

1. Transition Metals

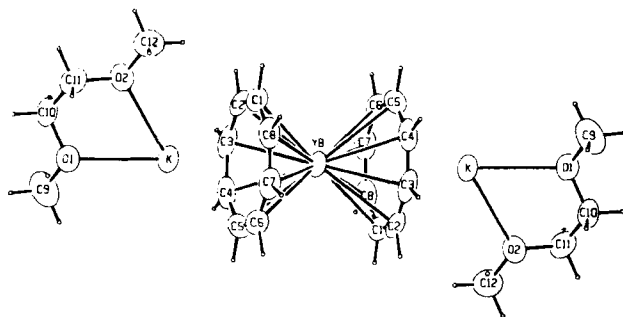
In contrast to the numerous lithium compounds in the mixed metal category, only a few structures with definite metal–carbon contacts have been described for the other alkali metals. These may be divided into two groups with respect to organoalkali coordination: Systems containing organic entities which exhibit π interactions (mostly ion pairs) and compounds with bridging phenyl groups (often clustered). Beside metal–carbon interactions we frequently encounter alkali–transition metal contacts. The high electron density at the d metals in these cluster cores facilitates interactions with alkali cations.

a. Polyhapto-Coordinated Alkali Sites. In $\text{K}(\text{diglyme})[\text{Ce}(\text{cot})_2]$ (**21**) (105) the coordination of the potassium ion is similar to that in the COT salts



described above: The solvated cation is located above the center of one of the COT rings of a $[\text{Ce}(\text{cot})_2]^-$ anion. The annulene ring shows large thermal motion along its circumference, perhaps indicating again rotation. [In $\text{U}(\text{cot})_2$, rotation of the COT rings in the crystal structure has been demonstrated by wide-line NMR (106).]

Reduction of this system gives $[\text{K}(\text{dme})]_2[\text{Ce}(\text{cot})_2]$ (107). While no detailed structure has been reported, a symmetrical triple ion pair is expected. [Perhaps these systems are better formulated as quadruple or quintuple ion pairs, since interactions within the $[\text{M}(\text{cot})_2]^{n-}$ unit are essentially ionic as well (108).] This was found for $[\text{K}(\text{dme})]_2[\text{Yb}(\text{cot})_2]$ (22) (108). The potassium—carbon coordination resembles that of other COT adducts. However, the chelating DME is unable to complete the coordination sphere of the large alkali cation: One additional oxygen contact to a DME molecule of a neighboring unit also is present.

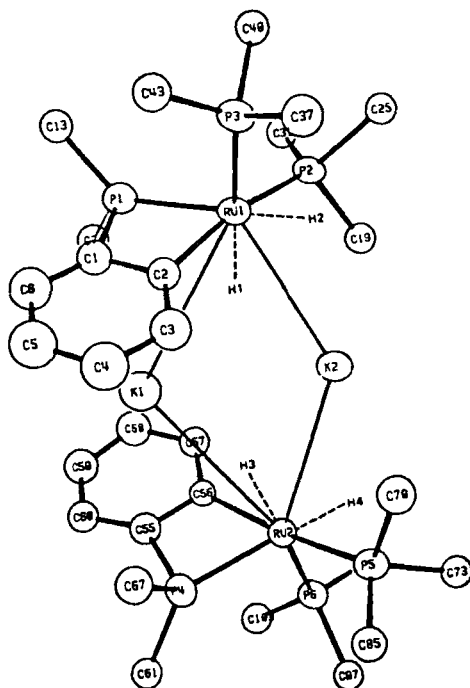


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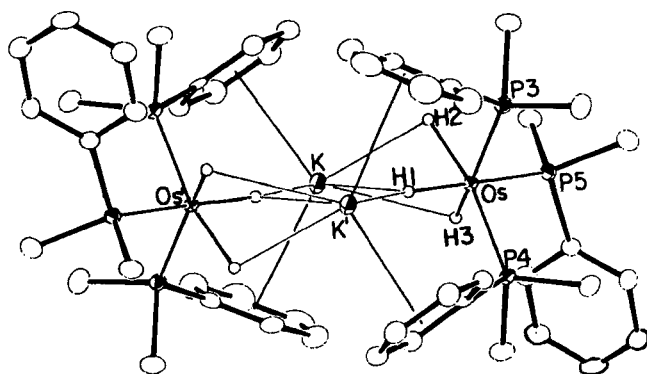
In the potassium hydridophosphine ruthenate complex **23** (109) two $[(\text{Ph}_3\text{P})_2\text{Ph}_2\text{PC}_6\text{H}_4\text{RuH}_2]^-$ units are connected via two potassium sites. One of these alkali ions is sandwiched between the aromatic systems of two ortho-metalated triphenylphosphino groups. The other K^+ cation is solvated similarly but less symmetrically by two phenyl rings. IR data as well as the geometries indicate strong $\text{K}-\text{H}$ contacts in both cases. Such interactions may explain an uncommon feature of this compound: Additional molecules capable of metal coordination (Et_2O , C_{10}H_8) are present interstitially in the crystal lattice, but show no alkali solvation at all.

Quite the same η^6 aromatic encapsulation of K^+ by the phenyl groups of phosphine ligands is observed in $\text{KOsH}_3(\text{PMe}_2\text{Ph})_3$ (24) (110); hydride anions occupy further coordination sites. The potassium coordination is completed by dimerization of two such intimate ion pairs. The K^+ —aromatic interactions again parallel findings on benzene-solvated potassium cations.

In another dimeric compound (111), $\{\text{K}[\text{Co}(\text{C}_2\text{H}_4)(\text{PMe}_3)_3]_2\}$ (25) the potassium ions are coordinated “side-on” by four transition metal-bound

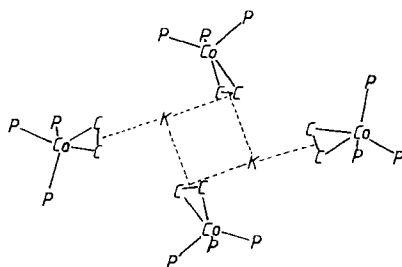


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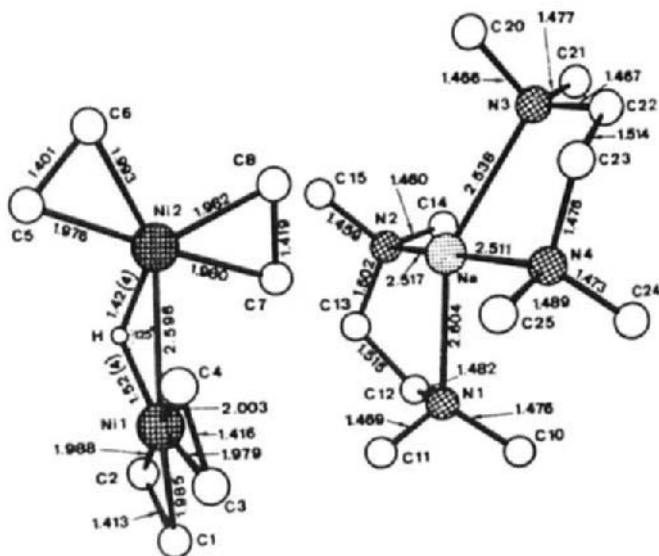
ethylene units. Each potassium interacts with two bridging and one terminal C_2H_4 moiety. The carbon- K^+ distances, 3.06 to 3.24 Å, correspond approximately to the sum of the ionic and van der Waals radii (112). However, the nature of the bonding involving the two “extra” electrons in **25** is not clear. Since graphite-potassium intercalates are formed easily from solutions of **25**,



25

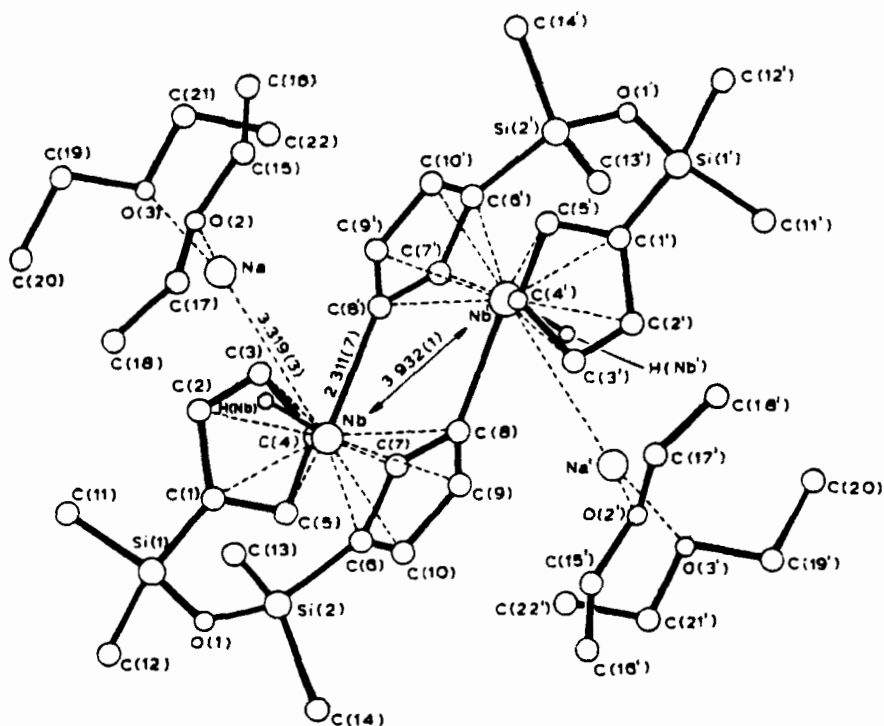
and no structural differences between the transition metal subunits exist, it has been proposed that **25** consists of solvated alkali atoms instead of ions. The related, though further reduced trimeric compound $\text{Li}[\text{Co}(\text{C}_2\text{H}_4)(\text{PMe}_3)_3]$ (*113*), exhibits the same kinds of olefin-alkali metal interactions.

These are found as well in the ion pair structure of $[\text{Na}(\text{tmeda})_2]\text{[Ni}_2(\text{C}_2\text{H}_4)_4(\mu\text{-H})]$ (**26**) (*114*), a formal addition product of NaH to $\text{Ni}(\text{C}_2\text{H}_4)_3$. Four coordination sites of the sodium ion are occupied by the chelating amine and the fifth by a η^2 -interacting ethylene unit of the metalate moiety. Related addition products of CH_3Li to olefin-nickel(0) complexes either do not exhibit such replacement of the lithium cation to the outside of the cluster (e.g., $[\text{Li}(\text{pmdta})][\text{Ni}(\text{C}_2\text{H}_4)_2(\text{CH}_3)]$ (*115*), or form solvent-separated ion pairs without Li-olefin interactions [e.g., $[\text{Li}(\text{tmeda})_2][\text{Ni}(\text{C}_2\text{H}_4)_2(\text{CH}_3)]$ (*166*)].



26

The structure of $[\text{Na}(\text{OEt}_2)_2][\text{Nb}_2\text{H}_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{OSiMe}_2\text{-}\eta^5, \eta^1\text{-C}_5\text{H}_3)_2]$ (**27**) (*117*) resembles lithium dianion structures like dilithionaphthalene-(*tmeda*)₂ (*97*), where the metals are on opposite sites of the ring system. The two ether-solvated sodium cations are positioned around the complexed transition metal dianion in an electrostatically favorable way. The principal interactions are to the metal centers and carbon atoms of the nestlike ligands.

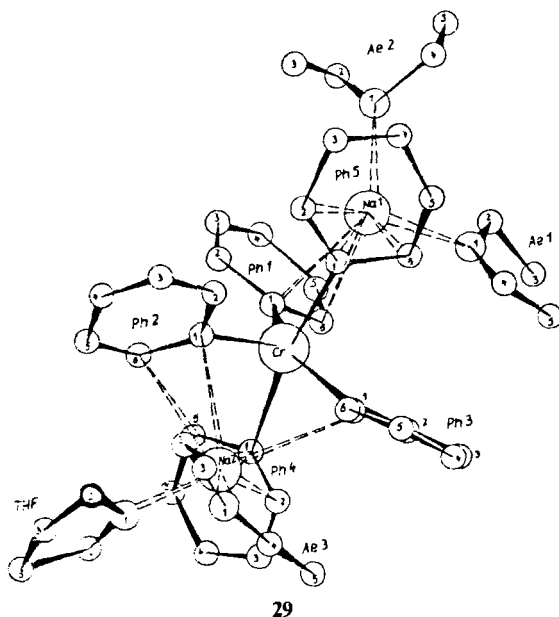


27

b. Systems Containing Bridging Phenyl Groups. Whenever alkali and transition metals both are involved in bridging to the same phenyl group, the interaction energy (and the covalent character) to the transition metal appears to be stronger. This is reflected by the way the phenyl groups tilt, as shown in Fig. 7, and varies, as expected, from Li to Cs.

Olefin-nickel complexes are known to react with a variety of organoalkali compounds (*7,115,118*). One such product, $[\text{Ph}_2\text{Ni}(\text{C}_2\text{H}_4)]_2\text{Na}_4(\text{thf})_5$ (**28**) (*119*), has a planar Na_2Ni_2 core surrounded by organic groups and two additional sodiums, solvated by THF. The inner core sodium ions are coordinated by one ether molecule, bridge two nickel atoms, and interact with

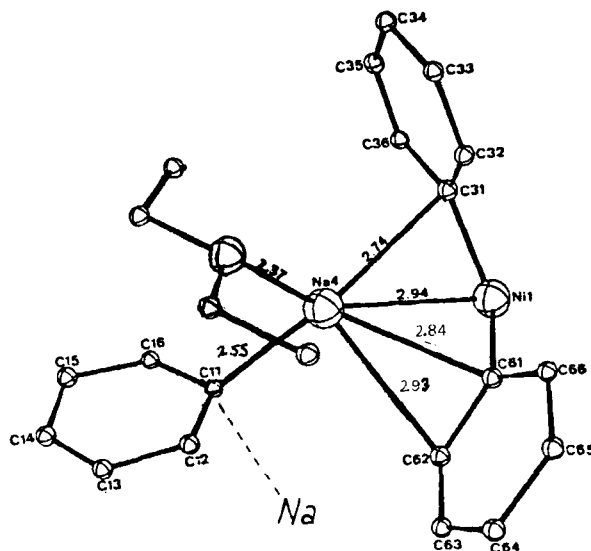
The structure of $\text{Na}_2\text{CrPh}_5 \cdot (\text{Et}_2\text{O})_3 \cdot \text{thf}$ (**29**) (120) involves a chromium atom, coordinated by five phenyl substituents forming a trigonal bipyramid. The ether solvated sodium atoms are stuck deeply into the spaces between the phenyl rings. However, instead of multihapto bonding (π -face complexation) they prefer to interact primarily with the phenyl α -carbon (which bears considerable negative charge) and some of the ortho positions as well. The resulting substructures again involve unsymmetrical bridging of two different kinds of metal atoms.



Two different alkali metals are present in a remarkable dinitrogen complex, $[\text{Na}_2\text{Ph}(\text{Et}_2\text{O})_2(\text{Ph}_2\text{Ni})_2\text{N}_2\text{NaLi}_6(\text{OEt})_4(\text{Et}_2\text{O})]_2$ (**30**) (121). The central cluster involves two $(\text{Ph}_2\text{Ni})_2\text{N}_2$ moieties linked together by two sodium atoms and two $\text{Li}_6(\text{OEt})_4 \cdot \text{OEt}_2$ units. Two $(\text{Na} \cdot \text{OEt}_2)_2\text{Ph}$ bridges are attached to the outside of this core.

Multiple metal–metal interactions occur in the central cluster. The oxygens coordinate mainly to the lithium ions; furthermore some lithiums contact phenyl groups as described above for the sodium structures. Two Li atoms are attached to the N_2 unit. The inner sodiums η_2 -bridge the dinitrogen unit and interact with two oxygens of ethoxide groups, as well as the transition metal, but not with any of the anions. Obviously, carbon interactions in the inner core are preferred by lithium, which localizes charge more effectively.

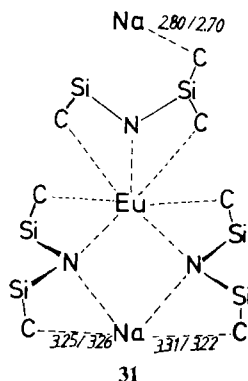
However, sodium–carbon interactions are involved in the outer regions of the structure, where bridging phenyl groups are to be found. Some of these are symmetrical and involve two sodium atoms, while some are unsymmetrical

Coordination of one of the outer sodium cations in **30**

and involve one sodium and one nickel. The latter exhibit increased carbon–sodium bond lengths (2.49 versus 2.77 Å, average values).

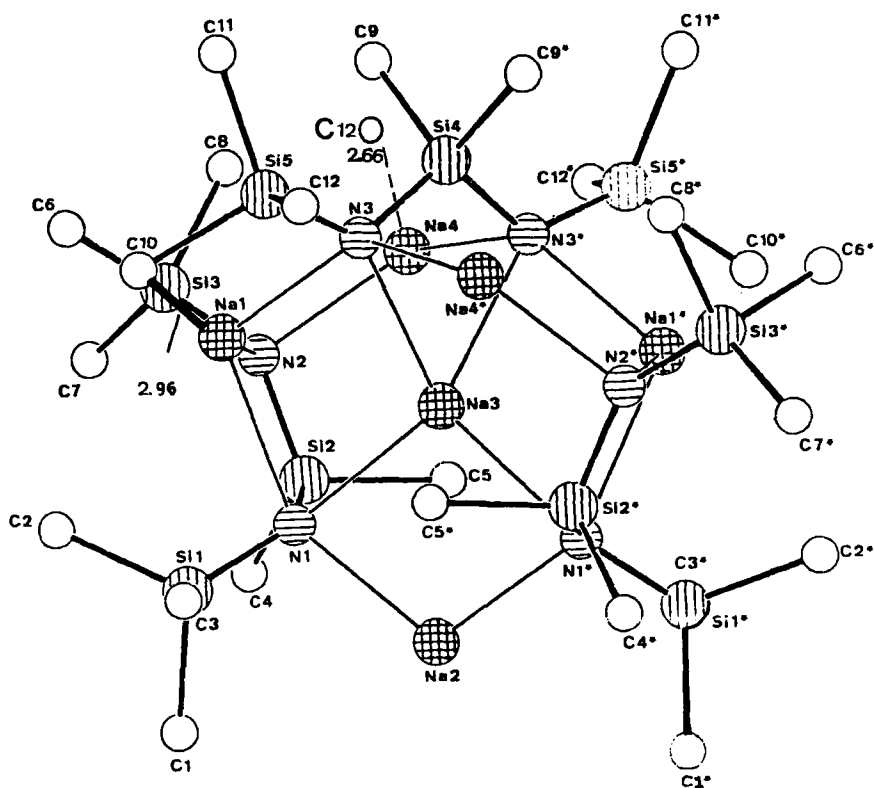
Why do the lithiums occupy some sites and sodiums other positions? The stronger binding of lithium to heteroatom ligands appears to be responsible. In analogy to the alkali distribution within this structure organosodium and lithium alkoxide compounds form from sodium alkoxides and organolithium derivatives via alkali metal exchange (122).

c. Divertimento. In two lanthanide compounds, $\text{NaEu}[\text{N}(\text{SiMe}_3)_2]_3$ (**31**) (123) and $\text{NaY}[\text{N}(\text{SiMe}_3)_2]_3$ (123), the main alkali coordination is achieved by bridges formed by two of the three silylamide ligands.



Additional interactions with methyl groups of trimethylsilyl units of neighboring complexes are present. This arrangement may not be due to any significant bonding between sodium and the surrounding methyl groups. NMR investigations only show one carbon or hydrogen signal at -80°C in hydrocarbon solvents. The three $\text{Si}(\text{CH}_3)_3$ methyls exchange rapidly. Similar alkali-carbon contacts were reported for a lithium compound, $\text{LiAl}[\text{N}=\text{C}(\text{tBu})_2]_4$ (124).

Even though the simple silylamide alkali compounds $\text{M}[\text{N}(\text{SiMe}_3)]_2$ [$\text{M} = \text{Li}$ (125), Na (126), K (127)] do not show such interactions, however, the related diamide dianion $\text{Na}_2[\text{Me}_3\text{SiN}(\mu\text{-SiMe}_2)\text{NSiMe}_3]$ (32) (128) exhibits appreciable binding between alkyl groups and the alkali cations. As α -silicon substituents are known to stabilize negatively charged centers by hyperconjugation (4a,129), the methyl groups gain electron density. Electrostatic interaction with Na^+ cations follow.



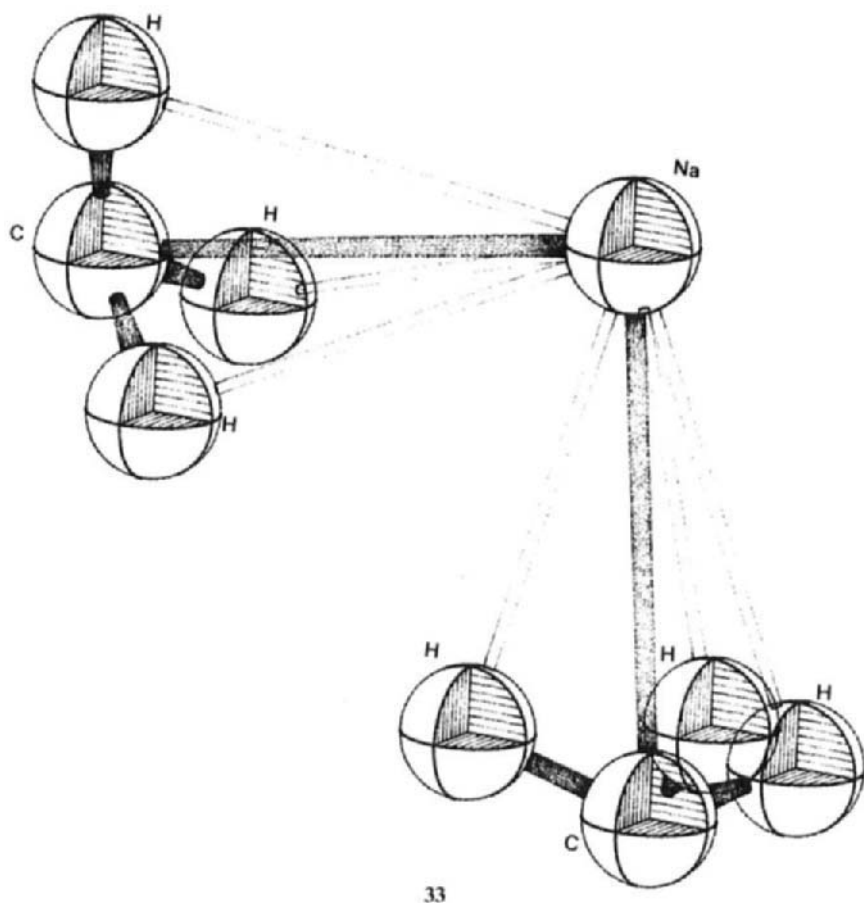
2. Main Group Metals

The variety of structures in this extensive group of compounds can be formulated as $R_nM^x \cdot R'M^1$ adducts where M^x is a group 2 or 13 metal, M^1 an alkali metal and R and R' are either "organic" or "inorganic" groups. For Ziegler–Natta-related compounds, rivalry between several types of carbon–metal bonding can take place. R' groups could either coordinate mainly to alkali atoms, bridge between the different metals, or be attached to the other metals. The last situation gives the "ate" complexes, $[R_nR'M^x]^-M^{1+}$, described by Wittig (130). Structures containing isolated tetracoordinate metalate anions and alkali cations, which fill interstices of the anion sublattice, often result. Only relatively weak alkali–carbon interactions occur in these three-dimensional network arrangements.

Hydrogen positions are reported in only a few examples; even then they are often assumed to involve "standard" geometries. However, as can be deduced from the structure of $Na[Al_2Me_6H]$ (33) (131), where the hydrogen positions are reasonably well established, the main alkali coordination sphere involves hydrogen contacts (Fig. 6, p. 185). The overall character is clearly that of an ate anion and sodium cation. The pentacoordinate carbon center is linearly coordinated by the two metal positions. However, even though moderate planarization of the methyl group is observed, it does not represent D_{3h} -like geometry (89). Lithium compounds approach this situation more closely, as is illustrated by the results of the neutron diffraction study of $Li[BMe_4]$ (132).

Alkali metal or even tetraalkylammonium substitution does not really affect the structural or spectroscopic (e.g., IR) data of such complex anions. In several of these compounds, the alkali counterions are solvated by aromatic π systems, which may often be reversibly introduced into the crystal lattices. This behavior helps demonstrate that the cations interact relatively weakly with the ate counteranions. Most of these species are quite reactive, but some like $Na[BPh_4]$ are water soluble. The ionic nature of these systems is shown by data in solution: $Na^+[BPh_4]^-$ exists as solvent-separated ions or ion pairs in THF, whereas "inorganic salts" like $NaClO_4$ or $NaSCN$ are contact ion pairs or higher aggregates (133). Even poorly chelating "ligands" such as $[Co(salen)]_2$ are able to separate the sodium ions from $Na^+[BPh_4]^-$ in the solid state or in solution (134).

However, in spite of this chemical behavior and spectroscopic data, which clearly indicate separated ate anions and alkali counteranions, the solid-state geometries do not substantiate this picture. The alkali metal–carbon bond distances are of about the same magnitude as in anions containing more conventional $M-C$ contacts. Rather few lithium structures (beside those of the related cuprates) are reported in this field, but these are quite similar to those discussed above. A tendency to form more distorted arrangements due to the smaller size of lithium can be noted.

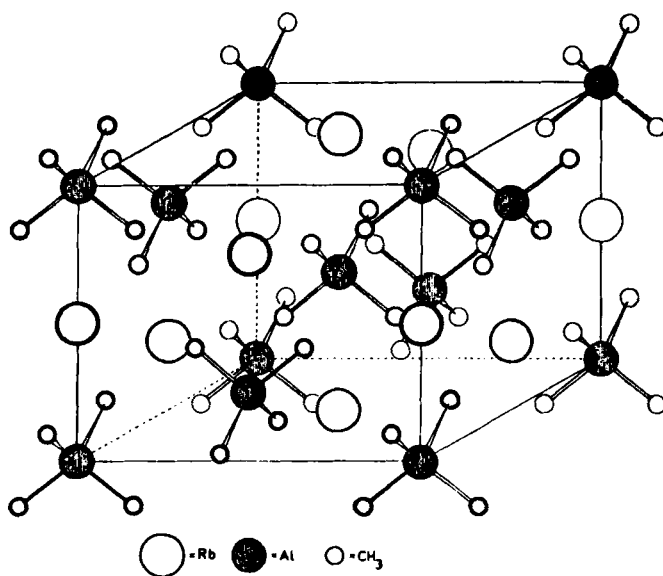


a. ate Complexes from Organoalkali Compounds. Generally, a tetrahedral arrangement (sometimes distorted) around the group 13 metal center of $[\text{R}_4\text{M}^{13}]^-\text{M}^{1+}$ compounds is adopted by the hydrocarbon ligands. Interactions of these complex anions with alkali cations differ only with respect to the presence of π systems or additional coordinating molecules.

i. Alkyl systems. Ion lattice-type structures are built up by the alkali cations and tetramethylmetalate anions of the following:

$\text{Na}[\text{AlMe}_4]$ (135)		$\text{Na}[\text{InMe}_4]$ (137)
$\text{K}[\text{AlMe}_4]$ (136)	$\text{K}[\text{GaMe}_4]$ (136)	$\text{K}[\text{InMe}_4]$ (138)
$\text{Rb}[\text{AlMe}_4]$ (136)	$\text{Rb}[\text{GaMe}_4]$ (136)	$\text{Rb}[\text{InMe}_4]$ (138)
$\text{Cs}[\text{AlMe}_4]$ (136)		$\text{Cs}[\text{InMe}_4]$ (138)

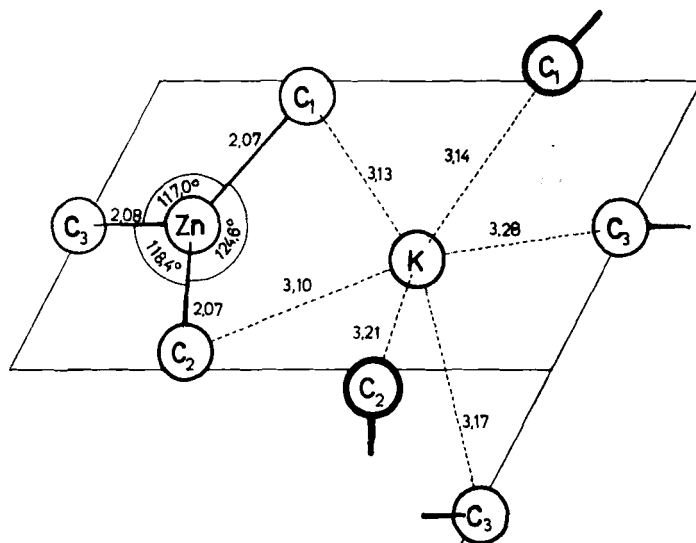
They crystallize in the same general structure **34**. Alkali ions are surrounded by eight carbon atoms from six different anions. $\text{Cs}[\text{InMe}_4]$ (coordination number [12]) and $\text{Na}[\text{InMe}_4]$ as well as $\text{Li}[\text{InMe}_4]$ ([4]) have slightly modified structures; the deviations are in line with the alkali metal size. The fourfold coordination by methyl groups in $\text{Na}[\text{InMe}_4]$ resembles that in NaCH_3 (65); however, carbon-metal bond distances are enlarged for the mixed metal compound (2.76 versus 2.60 Å). The ate anion in $\text{K}[\text{In}(\text{CH}_2\text{SiMe}_3)_4]$ (139) is tetrahedral as well; the K^+ environment is not described.



34

The anion-solvating capability of organometallic Lewis bases has been used for dissolving alkali-alkyl compounds. Crystallization from a solution of KCH_3 in $\text{Zn}(\text{CH}_3)_2$ gives $\text{K}[\text{ZnMe}_3]$ (**35**) (135,140). Though definite ZnMe_3 assemblies of approximate D_{3h} symmetry are present in the structure, the trigonal pyramidal methyl coordination around K^+ and the $\text{K}-\text{C}$ bond distances are equivalent to those in KCH_3 findings (58).

ii. *Aryl and alkynyl compounds.* In aryl and alkynyl compounds the alkali ions again occupy positions in the ate anion lattice. As usual, the cations are in contact with the centers of highest charge density, i.e., the α -carbons of organic groups. Further coordination is provided by the hydrocarbon π system. These interactions appear to be weak, as cations and anions are often separated easily.



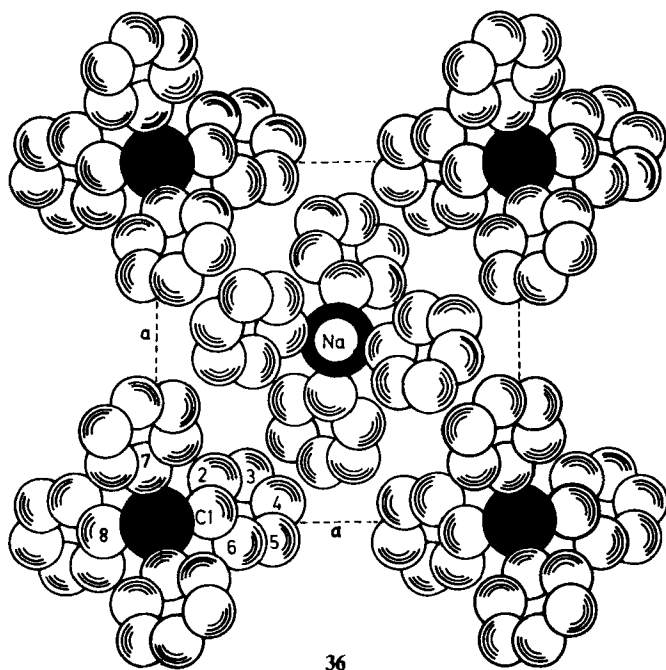
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The topologies of the Na, K (141), Rb (142), and Cs tetraphenyl boranate crystal structure are the same (143). The alkali ions are located among four phenyl groups of two different metalate anions. This approximately tetracoordinate environment is found in the related compound $\text{Na}[\text{InPh}_4]$ (36) (144) as well. A polynuclear lithium adduct, $[\text{Li}(\text{tmeda})]_2[\text{Mg}_2\text{Ph}_6]$, involves similar interactions (145). However, the smaller lithium prefers close MC contacts; aggregation as in the sodium compound (36) does not occur.

In two alkynyl compounds, $\text{K}_2[\text{Zn}(\text{C}\equiv\text{CH})_4]$ (37) and $\text{K}_2[\text{Cd}(\text{C}\equiv\text{CH})_4]$ (146), the potassium ions are coordinated by eight carbon atoms. Both α - and β -carbons of the alkynyl units possess similar distances to the alkali cation; hence η^2 coordination to the acetylenic π system is observed.

iii. *Compounds formally containing π -delocalized anions.* The compounds of this class can be regarded as to have butadiene dianion moieties, which coordinate 1,4 to a central aluminum core. The discrete, tetrahedrally surrounded aluminate anions are involved with two of these butadiene systems. Alkali metal interactions mainly occur with the π systems of the ligands and are of ion/induced local dipole character.

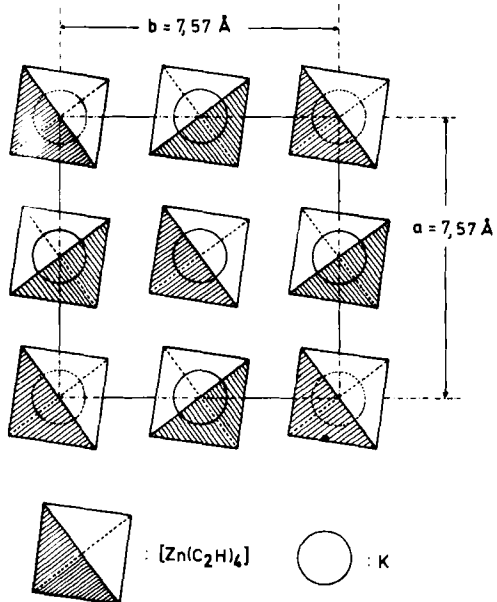
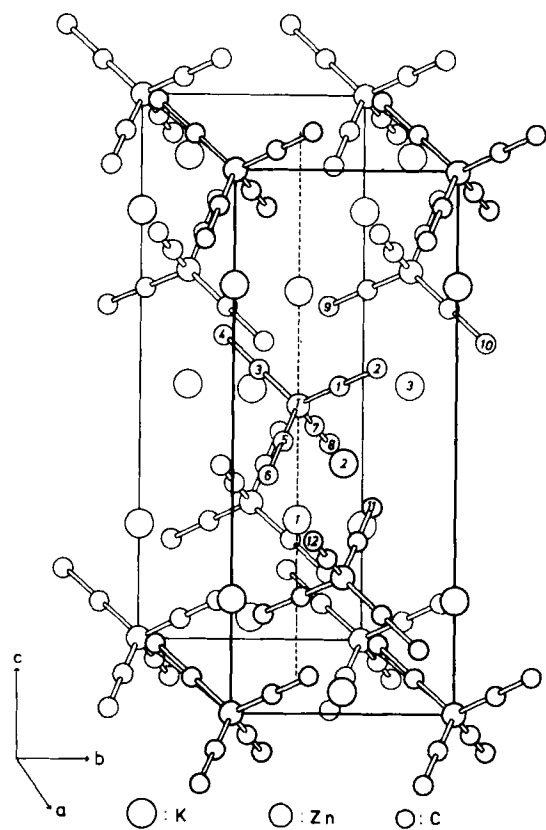
In the ion pair structures, $[\text{Na}(\text{thf})_2]_2[\text{AlMe}_2(\text{C}_{10}\text{H}_8)]_2$ (38) (147) and $[\text{Na}(\text{thf})_2]_2[\text{AlMe}_2(\text{C}_{14}\text{H}_{10})]_2$ (39) (148), THF-solvated sodium cations approach the π faces of the organic ligands. Bond distances are within the same range as to solvating aromatic molecules (e.g., 63). In $\text{K}[\text{Al}(\text{C}_8\text{H}_{12})_2]$ (40) (149) two COD entities are 1,4-bridged by aluminum. Unsolvated potassium



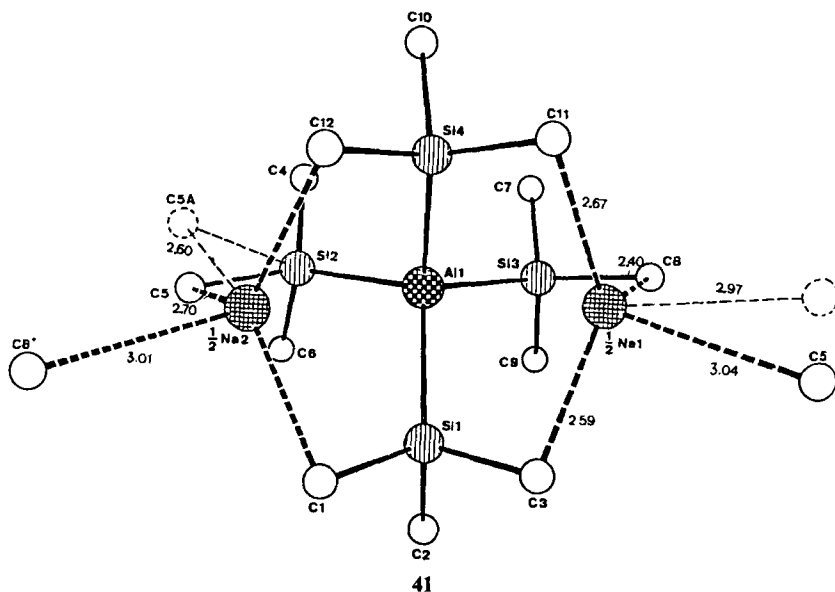
ions coordinate to the outside olefinic part of two roughly spherical aluminate anions. The structure of $K_2[Ca(cot)_2]$ (with and without additional DME ligands) has been shown from IR and X-ray powder data (108) to be isostructural with the ytterbium compound **22**, whose DME adduct is described on p. 209. (108).

b. ate Complexes from Nonorganic Alkali Compounds. Three features generally characterize the adducts of a main group organometallic and alkaline "inorganic" compounds. As discrete ate anions are formed, the alkali ions are stabilized poorly by the ligand's hydrocarbon substituents, since the M—C interactions are relatively weak. Hence, (1) Electronegative atoms tend to coordinate with the positive ions, but this may sometimes be prevented by steric hindrance. For example, in $M[AlMe_3CN]$ the alkali ion interacts with the nitrogen; the aluminum atom prefers C bonding (150). [However, *ab initio* calculations on MCH_2CN indicate 1,3-C,N bridging of the cations (4b).] (2) Crown ethers separate complex anions and alkali cations easily. (3) Aromatic π donors like benzene can be included in the crystal lattices where they form weak charge-induced dipole complexes with the alkali cations (8).

i. Trimethylsilyl compounds. $Na[Al(SiMe_3)_4]$ (151) exists in the solid both without and with 2 mol of toluene as additional coordinating ligand. In both



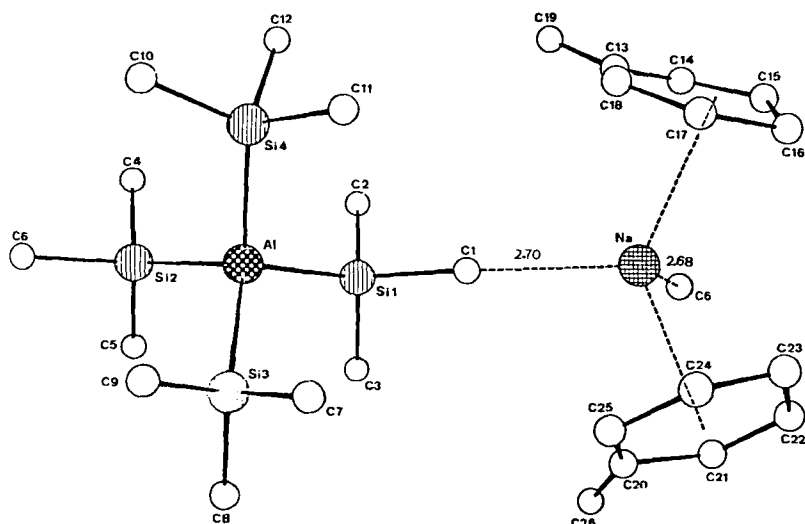
structures sodium is roughly tetrahedrally coordinated. In the solvent-free structure **41** the Na^+ contacts three methyl groups of three different SiMe_3 units of a single complex anion; the fourth coordination site is occupied by the residual SiMe_3 group of a neighboring anion.



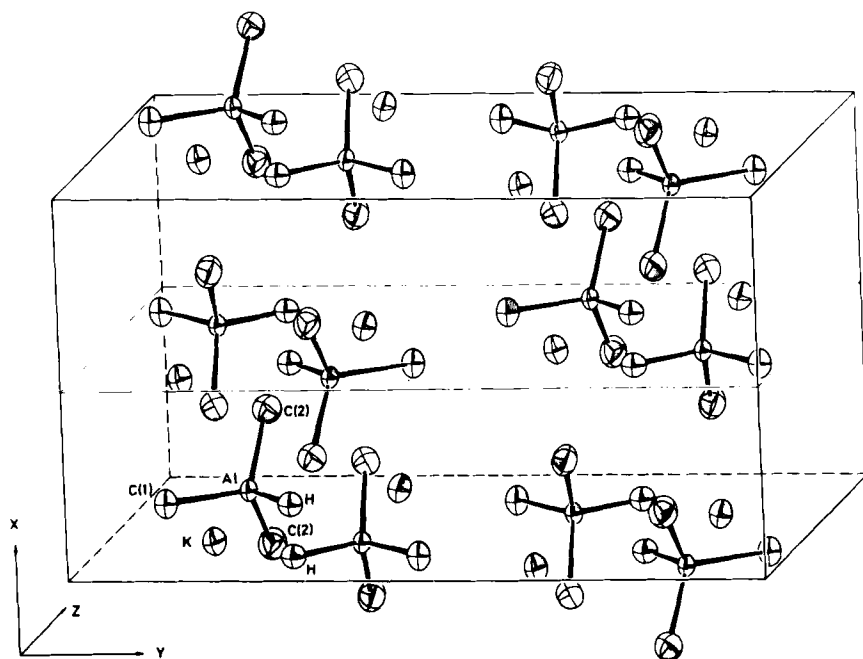
When the two toluene molecules are present (**42**), two tetrahedral positions are substituted by the η^6 -aromatic rings; however, the sodium ion still connects two anions with its further sites, and one-dimensional chains result. The incorporation of toluene solvent molecules does not alter the ate anion geometries at all, reflecting the weak cation-anion interactions in these compounds. However, the Na—C bond lengths are slightly increased (average: 2.60 Å in **41**, 2.69 Å in **42**).

ii. *Hydrides.* When H^- (formal hydride) ions are present, they will often coordinate or bridge alkali ions. Interestingly, sodium species often form clusters, whereas potassium systems crystallize in three-dimensional arrays. Thus $\text{K}[\text{AlMe}_3\text{H}]$ (**43**) (152) forms an open ion lattice; the potassium ions are loosely stacked between the complex anions. Only three K^+ contacts approach closer bonding distances (within 3 Å), two of these involve hydride ions.

$\text{K}[\text{Ga}(\text{CH}_2\text{SiMe}_3)_3\text{H}]$ (139) shows a similar three-dimensional network arrangement of discrete tetrahedral anions and interstitial cations. For $\text{Na}[\text{Al}_2\text{Me}_6\text{H}]$ (see **33**) (131), however, no alkali-hydride interactions are noted. Sodium is octahedrally coordinated by six methyl groups. A very

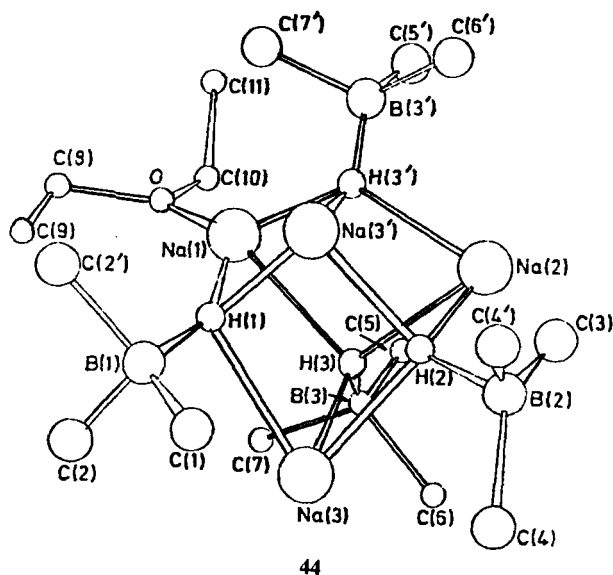


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distorted cubic cluster is adopted by the related system $(\text{Na}[\text{BMe}_3\text{H}])_4 \cdot \text{Et}_2\text{O}$ (**44**) (153). The inner core is formed by a Na_4H_4 unit. One sodium ion completes its coordination sphere by an ether molecule; the others are involved in remarkably short intermolecular interactions with alkyl groups of neighboring tetramers [2.56–2.73 Å, compared to 2.58–2.76 Å in CH_3Na (65) and 2.73 Å in $\text{Na}[\text{InMe}_4]$ (137)].

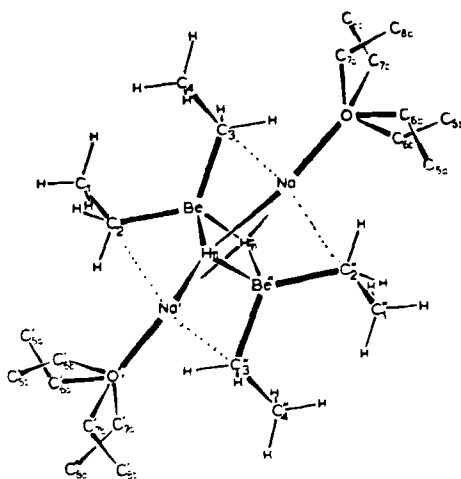


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For $(\text{Na}[\text{BeEt}_2\text{H}])_2 \cdot (\text{Et}_2\text{O})_2$ (**45**) (154) a dimeric unit comprised of $\text{Na}_2\text{H}_2\text{Be}_2$ atoms forms an octahedral array. Each sodium bridges between two hydride ions, is solvated by an ether molecule, and approaches the α -carbon of a beryllium-coordinating ethyl group as well.

Anions derived from carboranes may also be regarded as derivatives of ate anions. When cesium cations are involved, these species as well as their transition metallate complexes, generally avoid carbon–alkali contacts. However, the recently determined lithium carboranate structure of $[\text{Li}(\text{pmdta})][\text{Me}-\text{C}_2\text{B}_{10}\text{H}_{10}]$ (155), is characterized by strong bonding between lithium and electronegative carbon sites. Some structural features of these carborane compounds are listed in Section V.

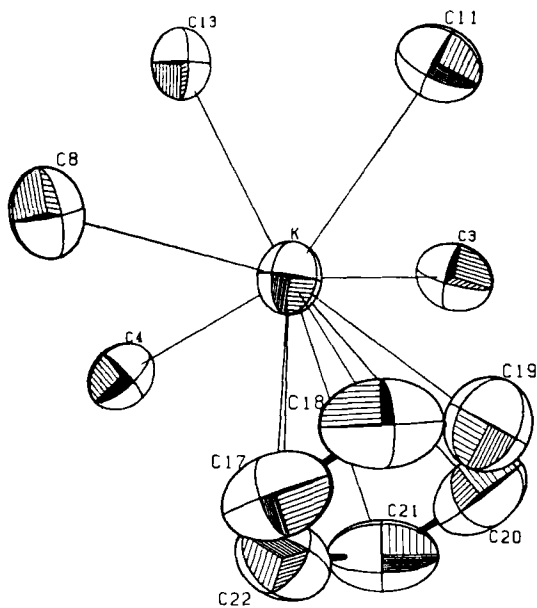
iii. *Alkoxides, selenides.* Depending on reaction conditions, potassium phenoxide and trimethylaluminum form two structurally characterized products. In $[\text{K}(\text{db-18-c-6})][\text{Al}_2\text{Me}_6\text{OPh}]$ (156) the potassium ion lies slightly above the coordination sphere formed by the crown ether, and is remote from all carbons. In $\text{K}[\text{AlMe}_2(\text{OPh})_2]$ (156), several carbon atoms are involved in



45

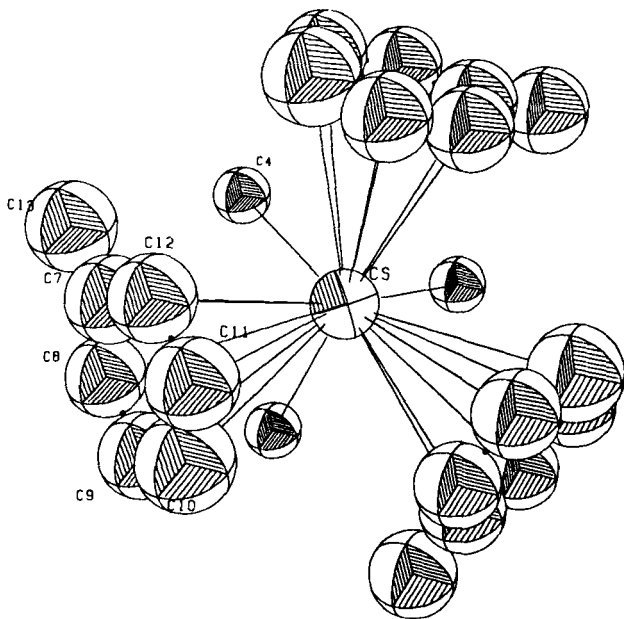
the alkali coordination sphere; the main interactions, however, again are provided by the alkoxide oxygen atoms.

Two methoxide adducts provide a comparison within the alkali group. The potassium ion in $\text{K}[\text{Al}_7\text{O}_6\text{Me}_{16}] \cdot \text{C}_6\text{H}_6$ (**46**) (157) is η^6 -coordinated by benzene. Five further contacts to methyl carbons complete the environment.



46

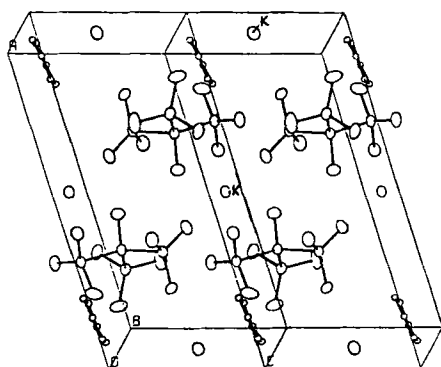
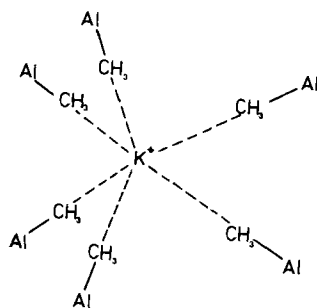
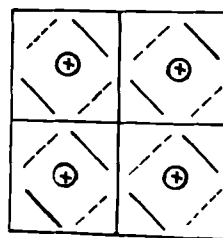
The larger cesium ion in $\text{Cs}[\text{Al}_7\text{O}_6\text{Me}_{16}]\cdot(\text{C}_6\text{H}_5\text{Me})_3$ (**47**) (8,157) is associated with three toluene units. The pseudooctahedral coordination is completed by three additional carbon contacts. The ionic radii rationalize the difference in average $\text{M}-\text{C}$ distances in both compounds. As oxygens are screened by bulky organoaluminum units, the otherwise preferred alkali-heteroatom contacts are probably inhibited.



47

The complex $\text{K}[\text{MeSe}(\text{AlMe}_3)_2]\cdot 2\text{C}_6\text{H}_6$ (**48**) (158) possesses two different alkali metal sites: In one potassium is packed within the methyl groups of four surrounding ate anions. In the other potassium does not interact at all with complex anions; instead, it is sandwiched among four benzene rings. The aromatic molecules exhibit much thermal motion. Two further, but rather remote carbon atoms complete the pseudooctahedral coordination. As with all other aromatic solvent molecules, the alkali-carbon distances are considerably larger (about 0.2–0.3 Å) than those in carbanion-cation combinations, where the electrostatic attractive forces are greater.

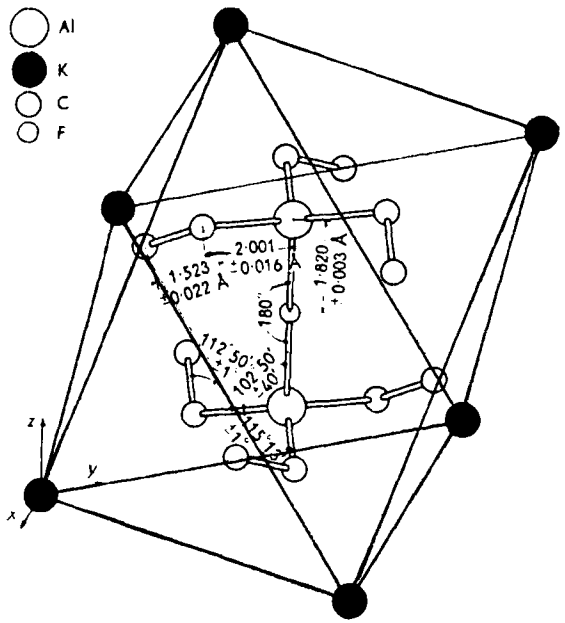
iv. Halides. $\text{K}[\text{Al}_2\text{Me}_6\text{F}]\cdot\text{C}_6\text{H}_6$ (**49**) (159) is formed by the reaction of KF with AlMe_3 in benzene. No $\text{K}-\text{F}$ interactions exist in the solid state; the potassium ion is nearly octahedrally surrounded by six different methyl groups from four ate anions. The benzene molecules merely occupy lattice vacancies and do not interact with the alkali ions ($\text{K}-\text{C}$ distances > 3.95 Å).

Pattern of the K^+ coordination by benzene ligands in **48****49**

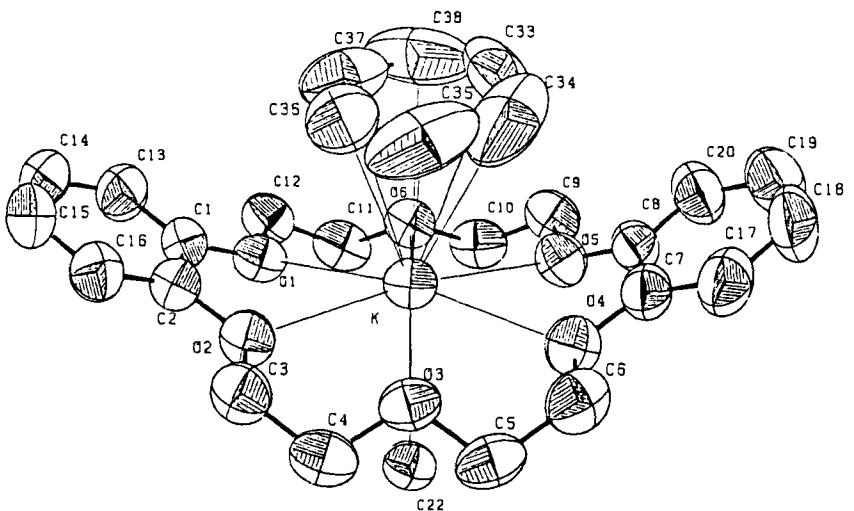
A similar, yet more regular situation was found for the compound $K[Al_2Et_6F]$ (**50**) (160). The potassium coordination may be envisioned as a distorted octahedron formed by six methylenes of the ethyl groups of different anions. These methylene groups have a partial negative charge due to the attachment to the rather electropositive aluminium. The related lithium compounds behave similarly. Remarkably, the fluorine heteroatom again is not involved in the alkali environment. While hydrogen positions are given, they were, alas, presumed to possess standard geometries—justified by a better R value—and thus cannot be used to really clarify the detailed nature of the alkyl group bridging.

The crown ether-coordinated potassium ion in $[K(db-18-c-6)][Al_2Me_6Cl] \cdot 2C_6H_6$ (**51**) (161) resides slightly above the plane of the ligand and, in addition, is solvated by a benzene molecule. The thermal parameters again indicate the possible rotation of the C_6H_6 ring.

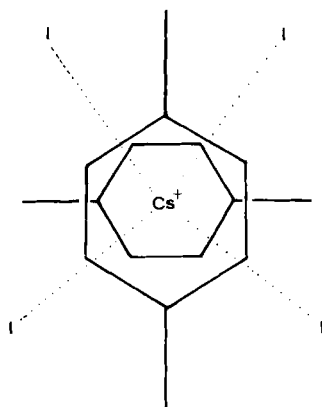
Finally, in $Cs[AlMe_2I_2] \cdot C_6H_4(CH_3)_2$ (**52**) (162) the cesium ion is sandwiched between two xylene molecules. The main interaction, however, seems



50



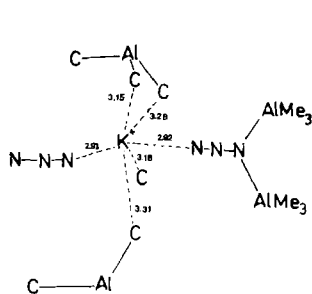
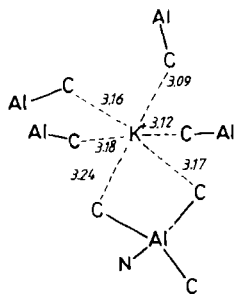
51



52

rather to be provided by heteroatoms, as four iodine atoms are arranged at the edges of a square around the central cation.

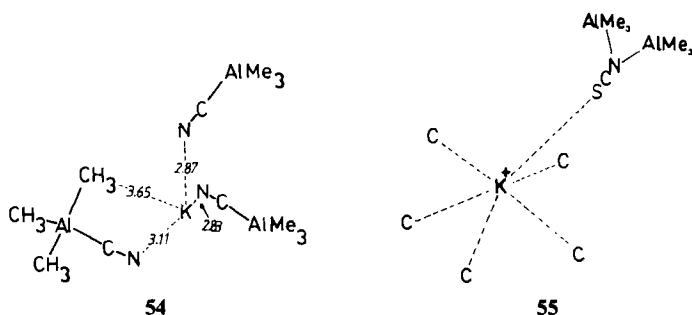
v. Pseudohalides. The reaction products of potassium, rubidium, and cesium azide with AlMe_3 have given rise to five different crystal structures. In the potassium salt **53** (163) two alkali metal sites are present. Two nonlinear $[\text{AlMe}_3\text{—N}_3\text{—AlMe}_3]$ units are associated with $\text{K}^+(1)$; there are two nitrogen contacts to different N_3 groups. Four methyl carbons complete the octahedral arrangement. The coordination at the second potassium site consists of six methyl groups only. Internuclear distances for this unit, however, are somewhat larger (~ 0.2 Å) than in simple hydrocarbon anions, quite characteristic for these substances.

Coordination of K-1 in **53**Coordination of K-2 in **53**

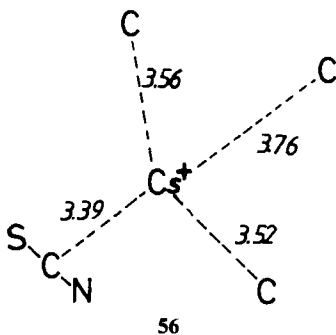
The rubidium adduct, $\text{Rb}[\text{AlMe}_3\text{N}_3]$ (164), contains only one AlMe_3 unit. Hence, far more favorable heterocoordination is achieved for the alkali cations. Two alkyl groups complete the coordination sphere, but do so only marginally. The same is true for $\text{Cs}[\text{AlMe}_3\text{N}_3]$ (165), where two methyl groups complete the distorted octahedral environment of the cesium cation.

If the same compound is synthesized from xylene, solvent molecules are included in the unit cell; in $\text{Cs}[\text{Al}_2\text{Me}_6\text{N}_3] \cdot (\text{C}_6\text{H}_4\text{Me})_2$ (8,166) the cesium cation is sandwiched between these two aromatic units.

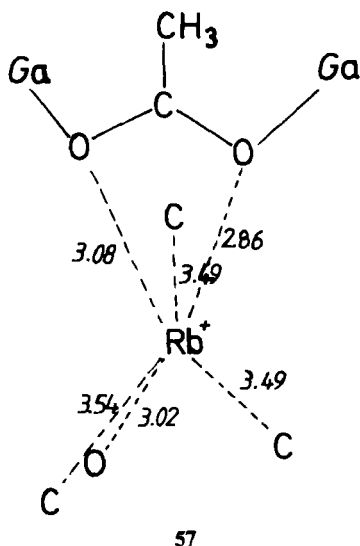
In $[\text{K}(\text{db-18-c-6})][\text{Al}_2\text{Me}_6\text{N}_3] \cdot (\text{C}_{11}\text{H}_9)_{1.5}$ (166), however, the potassium ions are crown ether coordinated only and do not interact with the π system of the 1-methylnaphthalene units. In $\text{K}[\text{AlMe}_3(\text{CN})]$ (54) (167) the cyanide carbon coordinates to aluminum and the nitrogen to potassium. Potassium interacts with three such nitrogens from different molecules; four methyl groups are farther away. Due to the coordination of AlMe_3 units to nitrogen in the SCN^- anion, the potassium counterion interacts preferentially with the sulfur in the corresponding crystalline compound (55) (168). However, five methyl units of adjacent anions approach the alkali site more closely than the sulfur. This is quite different than in 54.



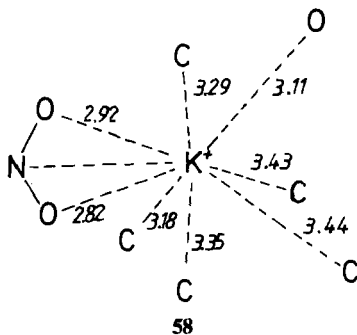
The nitrogen in $\text{Cs}[\text{AlMe}_3(\text{NCS})]$ (56) (169) also is involved in aluminum coordination. However, the alkali cation is located side on to the thiocyanate unit. Three methyl groups complete the environment of the alkali cation. Whereas $\text{K}[\text{GaMe}_3\text{NCS}] \cdot (\text{C}_6\text{H}_6)_{0.5}$ (8,170) shows no interaction with the aromatic cosolvent, one potassium site in $[\text{K}(\text{db-18-c-6})][\text{GaMe}_3\text{SCN}] \cdot (\text{C}_6\text{H}_6)_{2.5}$ (8) involves η^6 -coordination by one benzene ring.



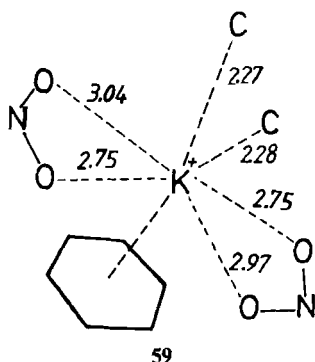
vi. *Oxoacid salts.* In $\text{Rb}[\text{Ga}_2(\text{CH}_3)_6(\text{CH}_3\text{COO})]$ (**57**) (171) each Me_3Ga moiety is attached to a different oxygen of the carboxyl group. This whole unit acts as a bidentate chelate toward the rubidium cation. Weak carbon and oxygen contacts to other ate anions supplement the psuedooctahedral coordination.



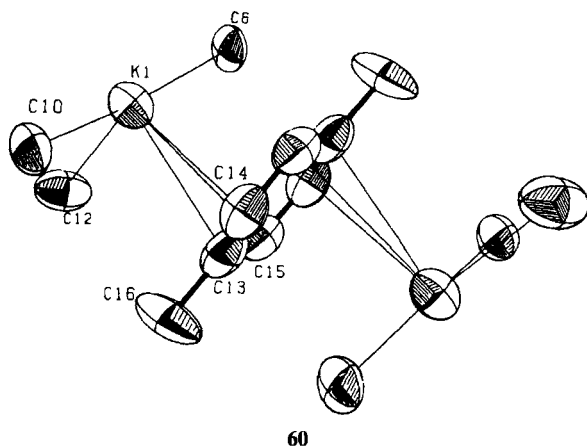
Adducts of KNO_3 with AlMe_3 form three different crystal lattices depending on the reaction conditions. This set of structures demonstrates nicely the weak bonding between the methyl groups and the alkali cation. In $\text{K}[\text{Al}_2(\text{Me})_6\text{NO}_3]$ (**58**) (172), the two similar potassium sites involve chelation by a bidentate nitro unit; carbon or oxygen positions complete the environment.



The related system $K[AlMe_3NO_3] \cdot C_6H_6$ (**59**) (172) possesses a π -solvating benzene molecule; two bidentate nitro and two methyl groups form the rest of the environment of the cation. The best potassium coordination is achieved upon crown ether addition. Thus, in $[K(db-18-c-6)][AlMe_3NO_3] \cdot 0.5C_6H_6$ (8,173) the benzene only completes the crystal lattice; heteroatoms surround the metal cation only.



$K_2SO_4/AlMe_3$ adducts have been characterized both with and without aromatic solvents: $K_2[Al_4Me_{12}SO_4]$ (174) and $K_2[Al_4Me_{12}SO_4] \cdot 0.5C_8H_{10}$ (**60**) (174). As in previous examples, two different potassium sites are present. One K^+ is mainly heterocoordinated by two oxygens, whereas the other ion has to be content with hydrocarbon environment. Interestingly, the *p*-xylene unit in $K_2[Al_4Me_{12}SO_4] \cdot 0.5C_8H_{10}$ bridges between two of the latter sites; the two K^+ are η^3 -positioned on different sides of the aromatic ring due to

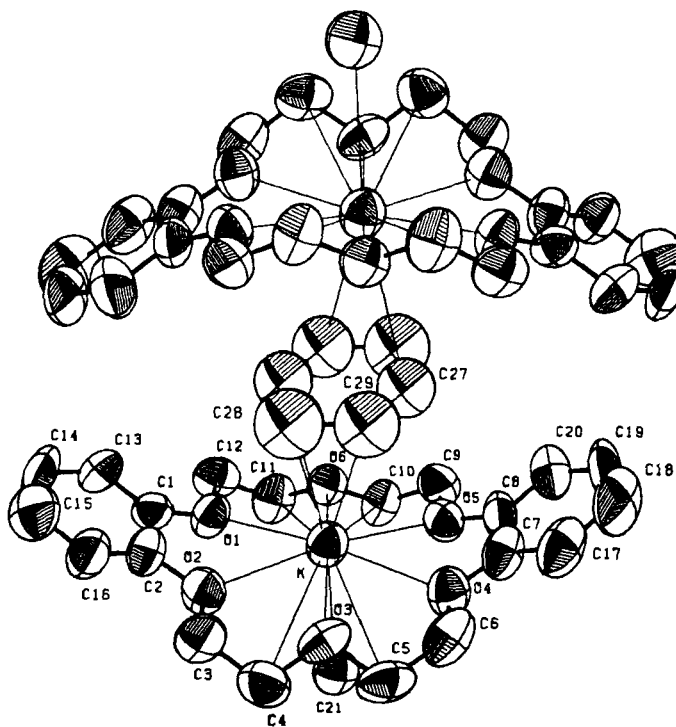


ion-induced dipole interactions. This resembles the situation seen in some cyclic "dianions."

In the analog $[\text{Cs}_2(18\text{-c-}6)][\text{Al}_3\text{Me}_9\text{SO}_4]$ (175) only oxygens surround the cesium counterions. While the Cs—Cs distance (3.92 Å) is only slightly longer than the sum of the ionic radii (3.38 Å), both ions are located on opposite sites of the crown ether plane.

vii. *Oxides.* In $[\text{K}(\text{db-}18\text{-c-}6)][\text{Al}_2\text{Me}_6\text{O}_2] \cdot 1.5 \text{ C}_6\text{H}_6$ (61) (8,176) two potassium sites are found. One of these involves a pair of crown-coordinated potassium cations separated by benzene. (The situation is similar to that in 60.) The cations are slightly moved out of the crown ether plane toward the solvent molecule.

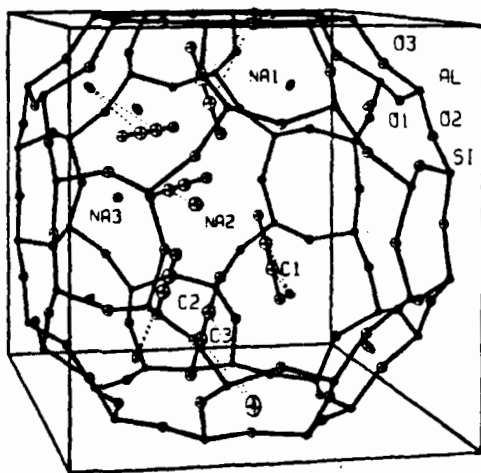
Several similar structures of ate complexes have been determined, but these generally do not possess close alkali metal-carbon distances: $\text{K}[\text{CH}_3\text{BF}_3]$ (177), $\text{K}[\text{CH}_3\text{AlCl}_3]$ (178), and the carboranate $\text{Cs}[\text{C}_5\text{B}_9\text{H}_{18}]$ (179), for example. The alkali coordination sphere of these as well as other adducts without carbon alkali contacts are summarized in Section V.



C. Ion-Dipole Complexes

In the last section we noted that aromatic molecules are often included in crystal lattices. Quite a few structures show alkali π system ion-induced dipole interactions. These are known theoretically (180) and experimentally [K^+/C_6H_6 , 19.2 kcal/mol (75); Li^+/C_6H_6 , 36.5 kcal/mol (72)] to involve considerable stabilization energy for alkali cations. For this reason, organo-alkali compounds commonly show enhanced solubility in aromatic than in aliphatic hydrocarbon solvents. Another manifestation of these interactions are found in zeolite adsorption complexes of unsaturated hydrocarbons. The heats of adsorption (i.e., for benzene in the range of 17 kcal/mol (181) parallel evaluated the gas phase alkali cation affinities.

The zeolite $4A \cdot (C_2H_2)_6$ complex (62) (182) involves η^2 -bonding of the acetylene molecules by the sodium cations of the aluminosilicate framework. The acetylene moiety deviates only slightly from linearity due to side-on Na^+ coordination. The same arrangement is predicted on the basis of *ab initio* calculations (183). The smallest $Na-C$ distances amount to about 2.6 Å ($3-21 + G//3-21 + G$: 2.72 Å), which is approximately the sum of the sodium ionic and the carbon van der Waals radii (112) (2.67 Å). This distance should be the lower limit for Na^+ solvation by polarizable neutral carbon systems. However, a few X-ray structures are known which actually show smaller alkali-carbon distances (see Table V).

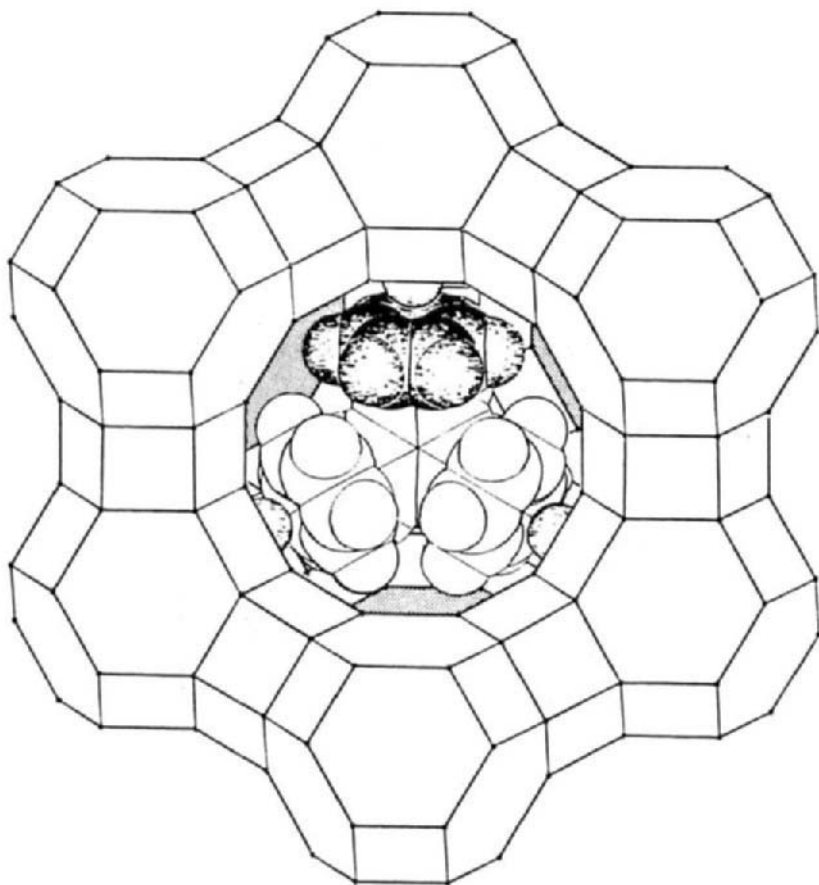


62

The same type of bonding has been verified for $Na-A$ -zeolite $\cdot (C_2D_2)_3$ (184) by neutron diffraction. Exposed sodium cation sites within the zeolite cavities again serve as adsorption sites. From IR studies, a similar side-on interaction

is found for K- and Ca-zeolite. At low temperatures even methane molecules in Na-A-zeolite·(CD₄)_x may be localized at the sodium positions (184). Enlarged Na—C distances and decreased heats of adsorption characterize this ion-induced dipole interaction. (Methane is less polarizable than hydrocarbons with π electrons.)

Recently, neutron powder diffraction has been used to determine the adsorption sites of (benzene)_x in a Y-zeolite (63) (185). Whereas one benzene site (I) is determined by van der Waals interactions with a Si₁₂O₁₂ polygon, the other site(II) involves η^6 -coordination by Na⁺. At low coverage ($x = 1.1$; I = 0.13, II = 0.83), the sodium positions are largely unchanged with respect to those in the bare zeolite. With increasing coverage ($x = 2.6$; I = 0.61, II = 2.48), the metal sites shift toward the benzene molecules, and lower



Na—C distances result. These are comparable to those observed for solvating hydrocarbons in organometallic species.

In potassium 1-(*N,N*-diphenylhydrazono)-2,4,6-trinitrobenzenide (186) the main metal interactions are with the heteroatoms, but two phenyl carbons are intermediate in distance to the cation. This may be due to stabilizing interactions with the π system or perhaps only to crystal packing effects. Similarly, in benzo-annelated crown ethers, the aromatic rings sometimes are face-oriented toward the alkali sites as if to participate in cation coordination (e.g., see Ref. 187). The rather large separations, however, do not suggest substantial interactions.

V

CARBANION STRUCTURES WITHOUT CARBON–METAL CONTACTS AND RELATED SYSTEMS

In this section we summarize briefly structures without carbon–alkali interactions, which nevertheless are formally derived from carbanions. The classification will follow the subdivision of Section IV; enolates and related structures are discussed in a separate section. The method of assignment of each structure is not without ambiguity, but allows related substances to be grouped together.

In general the following systems contain heteroatoms, N, O, Cl, and F, which are more electronegative than carbon. In addition, they are present in functional groups bound to the formally charge-bearing carbon center. The alkali ions only coordinate to these heteroatoms.

A. Carbanions Substituted by Electron-Withdrawing Groups

Since most of the species in this section are of the CX_3^- type, where X is an electron-withdrawing group ($-\text{CN}$, $p\text{-NO}_2-\text{C}_6\text{H}_4-$, etc.), a perhaps better description would be: "carbon centered, negatively charged particles." These weakly basic anions are often directly formed from aqueous solution; even some ammonium salts of these compounds exist (Table VII). Meisenheimer salts and cyclopentadienyl derivatives with highly electronegative ligands might be envisioned as π -delocalized compounds (structural data are summarized in Table VIII).

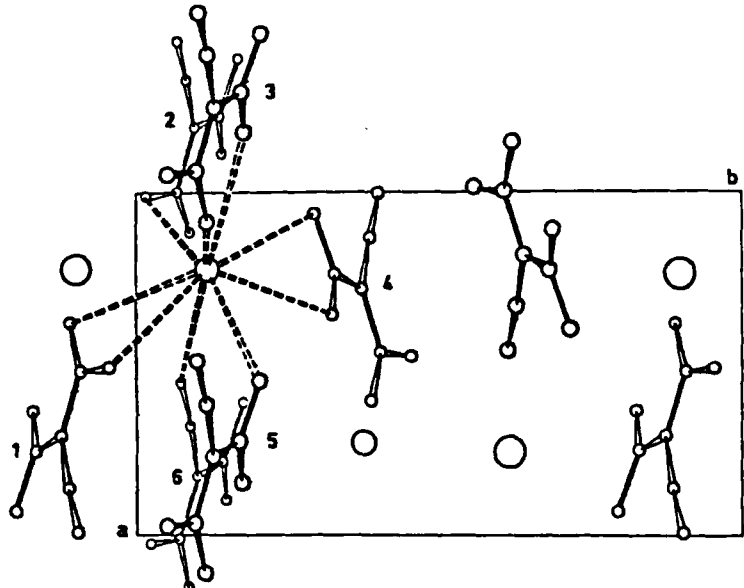
Quinoid systems are reasonably strong electron acceptors; their redox potentials also are determined by the substituents. Compounds which have electronegative groups are reduced easily by alkali metals. Radical anions often are produced; most of these are stacked in columns in the solid state, and

TABLE VII
SOME STRUCTURAL DATA OF "CARBANIONS" CONTAINING NO CARBON-ALKALI METAL INTERACTIONS

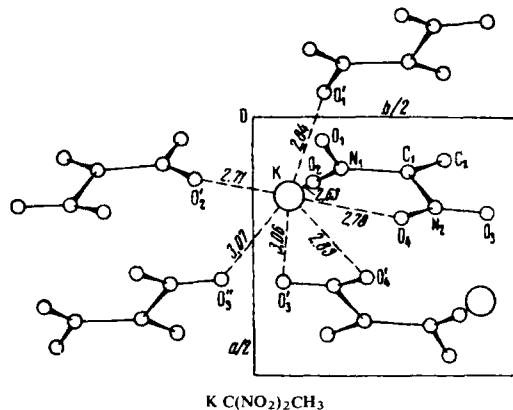
Compound	Coordination	Range (average) (Å)	Ref.
Na C(CN) ₃ (one bridging Na—C interaction reported: 3.11 Å)	N ₆	2.37–2.61 (2.51)	188
K C(CN) ₃	N ₇	2.85–2.98 (2.89)	189
K ₂ (CN) ₂ C—C(CN)C(CN)—C(CN) ₂	N ₇	2.79–3.42 (3.00)	190
K C(CN) ₂ —C(CH ₂ CN)—C(CN) ₂	N ₆	2.74–3.01 (2.88)	191
K C(CN) ₂ (<i>p</i> -NO ₂ —C ₆ H ₄)	O ₃ N ₇	KO: 2.78–2.87 (2.83) KN: 2.87–3.00 (2.91)	192
K C(CN) ₂ —COCH ₂ CN	N ₄ O ₂	KO: 2.72, 2.77 KN: 2.94–2.97 (2.95)	193
K C(CN) ₂ (3,5- ^t Bu-4-OH—C ₆ H ₂)·valinomycin	Crowned, not reported	KS: 3.19–3.35 (3.26)	194
Rb C(CN) ₂ (3,5- ^t Bu-4-OH—C ₆ H ₂)·valinomycin	Crowned, not reported	KN: 2.92–3.12 (3.01)	194
K C(CN) ₂ (NO)	Not reported	KO: 2.73	195
K ₂ C(CN) ₂ CS ₂ H ₂ O	S ₃ N ₃ O ₁	KS: 3.19–3.35 (3.26) KN: 2.92–3.12 (3.01) KO: 2.73	195a
K C(CN)(NO ₂)(Ph)	O ₃	2.69–2.74 (2.72)	196
K C(CN)(NO ₂) ₂	O ₈ N ₁	KN: 2.81 KO: 2.71–3.09 (2.93)	197,198

(continued)

TABLE VII (continued)

Compound	Coordination	Range (average) (Å)	Ref.
			
Rb $C(CN)(NO_2)_2$	O_8N_1	RbN: 3.20 RbO: 2.91–3.20 (3.09)	199–201
Cs $C(CN)(NO_2)_2$	O_8N_1	Not reported	199
K $C(NO_2)_3$	O_{10}	2.75–3.74	202,203
Rb $C(NO_2)_3$	Not reported		200,203

Cs	$C(NO_2)_3$	Not reported	203
K ₂	$C(NO_2)_2C(NO_2)_2$	O ₈	2.68–3.00 (2.82) 204,205
Rb ₂	$C(NO_2)_2C(NO_2)_2$	O ₈	2.83–3.14 (3.00) 204,206
K	$C(NO_2)_2H$	Not reported	207
Rb	$C(NO_2)_2H$	O ₇	2.84–3.07 (2.92) 207
Cs	$C(NO_2)_2H$	Not reported	207
K	$C(NO_2)_2CH_3$	O ₇	2.63–3.07 (2.85) 208



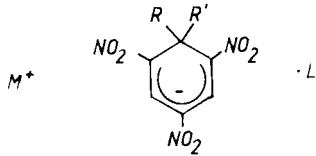
K	$C(NO_2)_2Ph$	O ₇	2.77–3.02 (2.87) 209
K	$C(NO_2)_2(p-ClC_6H_4)$	O ₇	2.69–3.02 (2.85) 210
K	$C(NO_2)_2[2,4,6-(NO_2)_3C_6H_2]$	O ₂ + O _{mult}	2.75, 2.90 ff. 211
Rb	$C(NO_2)_2[2,4,6-(NO_2)_3C_6H_2]$	O ₇	2.84–3.04 (2.99) 212
K	$C(NO_2)_2Br$	O ₄	2.69–2.86 (2.81) 213
Rb	$C(NO_2)_2CONH_2$	O ₆	2.96–3.11 (3.05) 214
K	$C(NO_2)_2CONHCH_3$	O ₆	2.71–2.88 (2.79) 215
Rb	$C(NO_2)_2CONMe_2$	O ₅	2.89–3.10 (3.00) 216
		O ₆	2.87–3.10 (2.95)

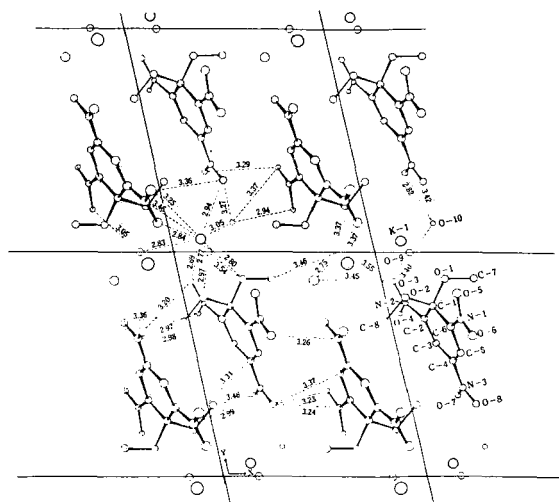
(continued)

TABLE VII (continued)

Compound	Coordination	Range (average) (Å)	Ref.
K $\text{C}(\text{NO}_2)_2\text{CH}_2\text{NHCOCH}_3$	O_6	2.78–3.03 (2.85)	217
K $\text{C}(\text{NO}_2)_2\text{CHCHCONH}_2$	O_8	2.63–3.21 (2.90)	218
K $\text{C}(\text{NO}_2)_2\text{CMe}_2\text{CN} \cdot \text{H}_2\text{O}$	O_6	2.76–2.94 (2.84)	219
Rb $\text{C}(\text{NO}_2)_2\text{CH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{CH}_2\text{COCH}_3$	O_5	2.85–3.00 (2.93)	220
K $\text{C}(\text{NO}_2)(\text{CONH}_2)_2$	O_7	2.72–3.06 (2.85)	221
K ₂ $\text{C}(\text{NO}_2)(\text{H})\text{COO}$	O_8	2.70–3.11 (2.87)	222
K $\text{C}(\text{NO})(\text{CONH}_2)_2$	O_8	(2.79)	223
Cs $\text{C}(\text{NO})(\text{CONH}_2)_2$	O_6	> 3.10	223
Rb $\text{CH}(\text{SO}_2\text{CF}_3)_2$	O_9	> 3.10	
	O_7	2.85–3.45	224
coordination sphere contains one carbon atom at 3.62 Å			
K $\text{C}(\text{SO}_2\text{F})_3$	O_8	2.74–3.12	225
Rb $\text{C}(\text{SO}_2\text{F})_3$	O_9	2.92–3.11 (3.04)	225
$[\text{K}(18\text{-c-}6)][\text{C}(\text{C}_6\text{Cl}_5)_3]$	O_6	2.74–2.85 (2.77)	226

TABLE VIII
SOME STRUCTURAL DATA OF CYCLOPENTADIENYL DERIVATIVES AND
MEISENHEIMER SALTS OF CARBANIONS

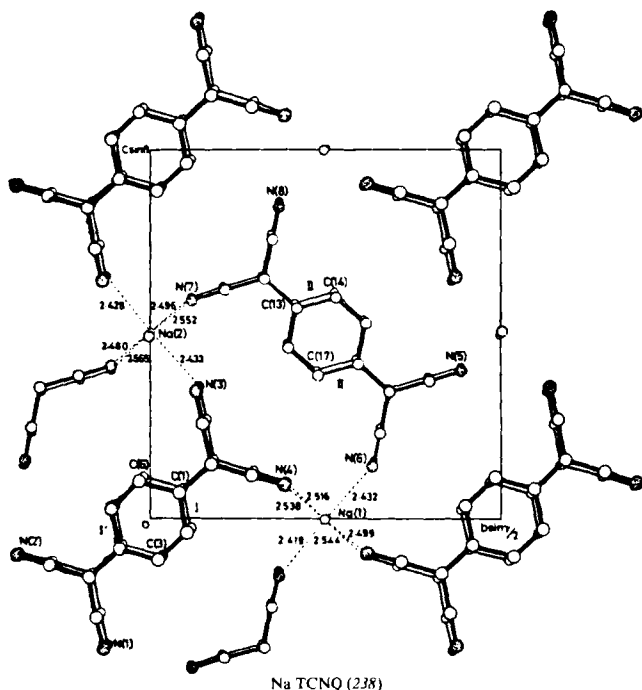
Compound		Coordination	Range (average) (Å)	Ref.
Cyclopentadienyl derivatives				
K C ₅ (NO ₂) ₂ Cl ₃		O ₆	2.58–3.38	227
K C ₅ (CO ₂ Me) ₅ ·MeOH		O ₆	2.65–2.86	228
<div style="text-align: center;">  </div>				
M	R	R'	L	
Meisenheimer salts				
K	H	OCH ₃	·(H ₂ O) _{0.5}	O ₈ 2.77–2.99 229
K	OCH ₃	OCH ₃	·(H ₂ O) ₂	O ₇ 2.69–3.05 230
K	OEt	OEt	—	O ₈ 2.71–3.13 231
Cs	OEt	OEt	—	O ₈ N ₁ CsO 3.13, 3.16 231
				CsN 3.38, 3.41
K	OCH ₃	COOCH ₃	—	O ₆ 2.74–2.93 (2.82) 232
K	H	CH ₂ COCH ₃	—	O ₆₊₂ 2.73–2.86 (2.79) 233
K	C ₈ H ₇ N ₄ O ₇	—	—	O ₄ (2.83) 234a,b
				O ₆ (2.90)
(4-Methoxy-5,7-dinitrobenzofurazan potassium methoxide adduct)				
K	C ₈ H ₇ N ₄ O ₈		O ₇	KO: 2.72–2.85 (2.79) 234c
(4-Methoxy-5,7-dinitrobenzofurazan-3-oxide potassium methoxide adduct)				



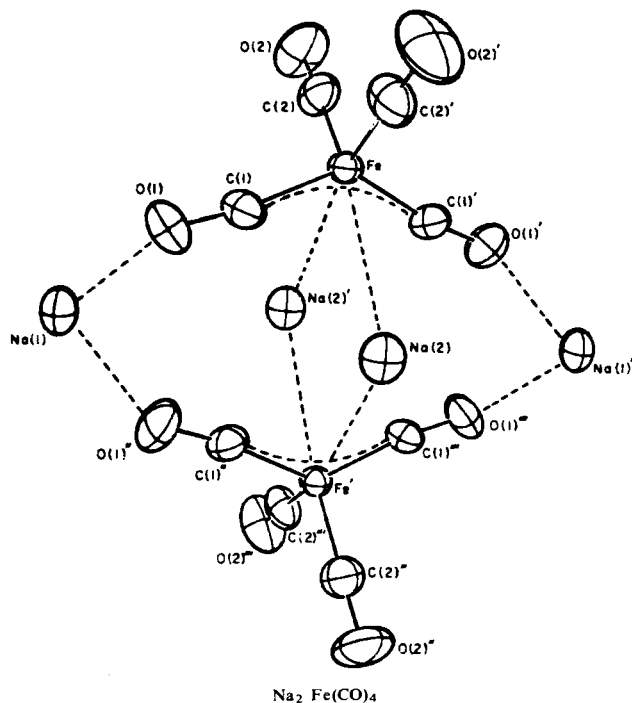
K 1,1-(OCH₃)₂-2,4,6-(NO₂)₃-C₆H₂·(H₂O)₂ (230)

TABLE IX

Compound	Coordination	Range (average) (Å)	Ref.
Biphenyl radicalanions			
Na C ₁₂ H ₁₀ •(tetraglyme) ₂	O ₈	2.50–2.76 (2.58)	100
K C ₁₂ H ₁₀ •(tetraglyme) ₂	O ₁₀	2.82–3.05 (2.93)	101
Rb C ₁₂ H ₁₀ •(tetraglyme) ₂	O ₁₀	2.93–3.15 (3.02)	102
Chloranil compounds			
α-K (C ₆ O ₂ Cl ₄)	O ₄	2.58–2.68	235
β-K (C ₆ O ₂ Cl ₄)	Not reported		235
K (C ₆ O ₂ Cl ₄)•acetone	O ₃	2.68–2.85	236
Tetracyanochinodimethane compounds			
Na TCNQ (high temperature)	N ₆	2.43–2.57 (2.49)	237
Na TCNQ (low temperature)	N ₆	2.42–2.56 (2.49)	238
K TCNQ (I) (high temperature)	N ₈	2.87–2.98 (2.92)	239
K TCNQ (II) (high temperature)	N ₈	2.90–3.00 (2.94)	240
K TCNQ (low temperature)	N ₈	2.86–3.03 (2.93)	240
Rb TCNQ (I) (high temperature)	N ₈	2.98–3.11 (3.04)	241
Rb TCNQ (II) (high temperature)	Not reported		242
Rb TCNQ (I) (low temperature)	N ₈	(3.08)	243
Rb ₂ (TCNQ) ₃ (high temperature)	N ₈	2.89–3.40 (3.17)	244
Rb ₂ (TCNQ) ₃ (low temperature)	N ₈	2.89–3.35 (3.14)	245
Cs ₂ (TCNQ) ₃	N ₈	3.07–3.49 (3.31)	246



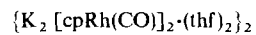
Compound	Coordination	Range (average) (Å)	Ref.
Carbonyl derivatives			
$[\text{Na}(2,2,2\text{-crypt})][\text{Co}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu_2\text{-CO})_2]$	N_2O_4	NaO (2.58) NaN 2.96, 2.67	247
Na $[\text{Co}(\text{CO})_4]$	O_4	NaO 2.33, 2.34 NaC 3.00–3.26	248
$\text{Na}_2\text{Fe}(\text{CO})_4 \cdot (\text{dioxane})_{1.5}$	Na-1 O_6 Na-2 O_2	NaO 2.32–2.99 NaO 2.25, 2.54	249



(continued)

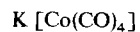
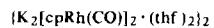
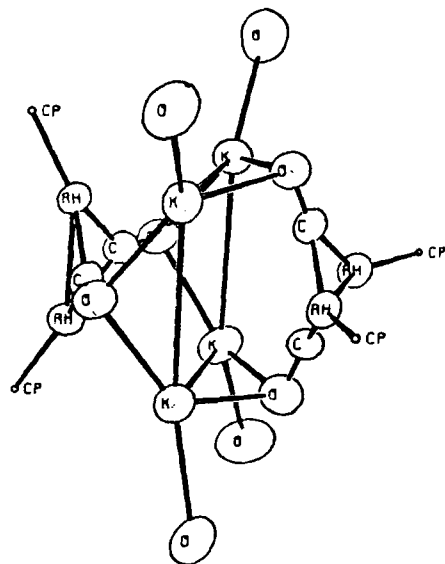
TABLE X (continued)

Compound	Coordination	Range (average) (Å)	Ref.
[Na(thf) ₂] ₂ [Zn(Fe(CO) ₄) ₂]	O ₆	NaO 2.31–2.57	250
[Na(thf) ₂] ₂ [Hg(Fe(CO) ₄) ₂]	O ₅	NaO 2.26–2.32 (2.28)	251
[Na(2,2,2-crypt)] ₂ [Fe(CO) ₄]	O ₆ N ₂	NaO (2.53)	252
		NaN 2.80	
[Na(2,2,1-crypt)][W(CO) ₅]	Crowned		253
[Na(18-c-6)][Rh(CO) ₃ (PPh ₃)]	O ₇	Not reported	254
[Na(thf) ₂][Rh(CO) ₂ (diphos)]	O ₃	Not reported	254
{[NaCo(CO) ₄ (THF)][Co(salen)] ₂ }	O ₆	NaO (2.42)	255
[Na(THF) ₂][Fe(CO) ₅ (COCH ₃)(μ ₂ -PPh ₂) ₂]	O ₅	NaO 2.23–2.45 (2.36)	256
[Na(2,2,1-crypt)][Cr(CO) ₅ (SH)]	O ₃ N ₂	NaO 2.39–2.47	257
		NaN 2.59, 2.61	
[Na(18-c-6)][W(CO) ₅ (SH)]	O ₇ S ₁	NaO 2.41–2.91 (2.70)	258
		NaS 3.01	
[Na(18-c-6)][W ₂ (CO) ₁₀ (μ-SH)]	O ₈	NaO 2.43–2.72 (2.59)	258
[Na(2,2,1-crypt)][W(CO) ₅ (O ₂ CH)]	O ₆ N ₂	NaO 2.39–2.60	259
		NaN 2.74	
[(Ph ₃ P) ₂ N] ₃ {Na[Mo ₃ (CO) ₆ (NO) ₃ (μ ₂ -OCH ₃) ₃ (μ ₃ -O)] ₂ }	O ₆	NaO (2.42)	260



KO Not reported

261

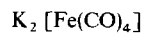


KK 4.08

KO 3.41–3.61 (3.48)

262

KC 3.41–3.93



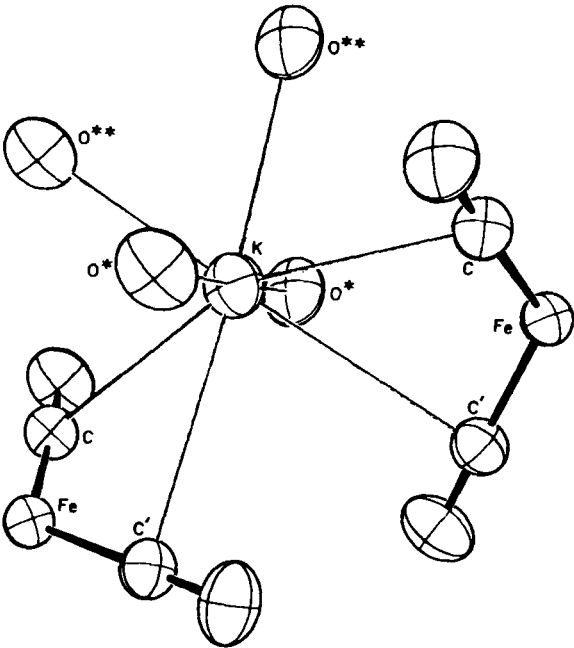
KO 2.71–3.80

252

KC 3.28, 3.40

(continued)

TABLE X (continued)

Compound	Coordination	Range (average) (Å)	Ref.
$[\text{K}(2,2,2\text{-crypt})][\text{HCr}_2(\text{CO})_{10}]$	Crowned		262a
 <p style="text-align: center;">$\text{K}_2 \text{Fe}(\text{CO})_4$</p>			
$[\text{K}(2,2,2\text{-crypt})][(\eta^5\text{-C}_5\text{Me}_5)\text{CoNi}_2(\eta^5\text{-cp})_2(\mu_3\text{-CO})_2]$	O_6N_2	KO (2.80) KN 2.99	263
$[\text{K}(2,2,2\text{-crypt})][\text{Ni}_3(\eta^5\text{-C}_5\text{H}_5)_3(\mu_3\text{-CO})_2]$	O_6N_2	KO (2.79) KN 2.98	263

$[\text{K}(18\text{-c-}6)][\text{Fe}_4(\text{AuPEt}_3)(\text{CO})_{13}]\cdot\text{CH}_2\text{Cl}_2$	O_8	KO 2.75–2.82	264
$[\text{K}(18\text{-c-}6)]\{\text{Rh}(\text{CO})_2[\text{P}(\text{OPh})_3]\}$	O_7	Not reported	254
$\text{Rb}[\text{Co}(\text{CO})_4]$	O_4	RbO 3.35–3.87 (3.51)	262
		RbC 3.36–3.87	
$\text{Cs}[\text{Co}(\text{CO})_4]$	O_4	CsO 3.11	265
		CsC 3.74, 3.84	
$[\text{Cs}_9(18\text{-c-}6)_{14}][\text{Rh}_{22}(\text{CO})_{35}\text{H}_x][\text{Rh}_{22}(\text{CO})_{35}\text{H}_{x+1}]$		Cs(1)O ₈	265a
		Cs(2)O ₁₂	
Carborane Complexes			
$\text{Cs Cr}(\text{Me}_2\text{—B}_9\text{C}_2\text{H}_9)_2\cdot\text{H}_2\text{O}$	No observable interactions within 4 Å		266
$\text{Cs Co}(\text{B}_9\text{C}_2\text{H}_{11})_2$	H_{10}	3.00–3.34	267
$\text{Cs Co}(\text{C}_5\text{H}_5)(\text{B}_7\text{CH}_8)$	Only three H contacts below 4 Å	(3.81)	268
$\text{Cs}_2[\text{Co}_2(\text{B}_9\text{C}_2\text{H}_4)_2(\mu\text{-B}_8\text{C}_2\text{H}_{10})]\cdot\text{H}_2\text{O}$	H_9O_1	CsH 2.82–3.29 (3.10)	269
	H_7O_1	CsO 3.03, 3.16	
$\text{Cs Re}(\text{B}_9\text{C}_2\text{H}_{11})(\text{CO})_{23}$	O_3	(3.2)	270
$\text{Cs}_2\text{Fe}_2(\text{B}_9\text{C}_2\text{H}_{11})_2(\text{CO})_4\cdot\text{H}_2\text{O}\cdot\text{acetone}$	O_{mult}	> 3.11	271
$\text{Cs}[\text{Co}(\text{C}_2\text{B}_9\text{H}_{10}\text{I})_2]$		CsH 2.95	271a
		CsB 3.70	
$\text{Cs}[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})(\text{C}_2\text{B}_9\text{H}_{10}\text{I})]$		CsH 2.87	271b
		CsB 3.58	
$\text{Cs}[\text{Co}(\text{C}_2\text{B}_9\text{H}_8\text{Br}_3)_2]$		CsH 3.08	271c

(continued)

TABLE X (continued)

Compound	Coordination	Range (average) (Å)	Ref.
Zeise salts			
K [PtCl ₃ (C ₂ H ₄)]·H ₂ O	O ₂ Cl ₆	KO 2.76, 2.80 (2.78) KCl 3.20–3.77 (3.44)	272,273
K [PtBr ₃ (C ₂ H ₄)]·H ₂ O	O ₂ Br ₆	KO 3.04, 3.23 KBr 3.16–3.80 (3.51)	273
K [PtCl ₃ (C ₂ H ₄)]	Cl ₆	3.14–3.24 (3.20)	274
K {PtCl ₃ [(Et) ₂ (OH)CC≡CC(OH)(Et) ₂]}	O ₂ Cl ₄	KCl (3.17) KO (2.73)	275
K {PtCl ₃ [(Et)(Me)(OH)CC≡CC(OH)(Me)(Et)]}	O ₂ Cl ₅	KCl (3.21) KO (2.74)	276
Others			
[Na(dme) ₂][Pr(C ₅ Me ₅) ₂ Cl ₂]	O ₄ Cl ₂	NaCl 2.76–2.87 (2.81) NaO 2.40–2.54 (2.43)	276a
Na ₃ {Co(cp)[P(O)(OEt) ₂] ₃ ·(H ₂ O) ₂ }	O ₆	NaO 2.28–2.36	276b
[Na(18-c-6)(thf) ₂][Nb(<i>o</i> -CH ₂ C ₆ H ₄ —C ₆ H ₄ CH ₂)(η ⁵ -cp) ₂]	O ₈	NaO 2.28–2.80	277
[K(18-c-6)][Mo(η ⁵ -C ₅ H ₅) ₂ (μ-H)]	O ₆ H ₁	KO 2.85–2.94 (2.88)	278a
[Na(15-c-5)][WH ₅ (PMe ₃) ₃]	O ₅ H ₃	NaO 2.46–2.66 (2.52)	278b
[K(18-c-6)][WH ₅ (PMe ₃) ₃]	O ₆ H ₃	KO 2.81–2.95 (2.88) KH (2.78)	278b
[K(18-c-6)][RuH ₃ (PPh ₃) ₃]	O ₆ H ₃	Not reported	278c
K _{0.58} Zr ₆ I ₁₄ C	I ₁₂	KI 3.71–4.18	279
Cs Zr ₆ I ₁₄ C	I ₁₂	CsI 3.83–4.19	279
K ₄ [Pt(P ₂ O ₅ H ₂) ₄ (CH ₃)(I)]·(H ₂ O) ₂	O ₈	KO 2.82–3.03	280

remarkable electronic conductivity may result. Lithium (and to some extent sodium) compounds again show deviations with respect to some of the physical properties from those of the heavier alkali metals (Table IX).

B. Transition Metal Complexes

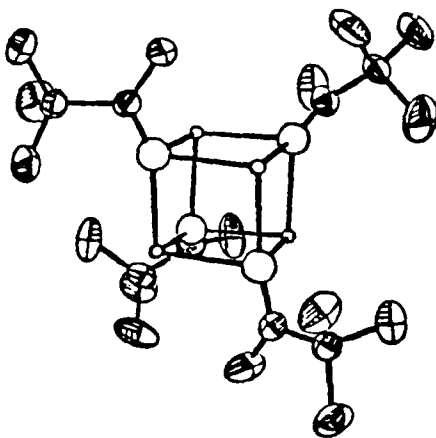
Transition metal complexes are illustrated by carbonylmetalates, carborane-based species, and Zeise salt analogs (Table X). In carbonyl complexes the alkali cations are attached chiefly to the oxygen periphery; for the carborane adducts cesium cations are barely coordinated within 4 Å. In Zeise-like compounds no alkali solvation by the olefinic system is observed; heterodonors provide a better coordination sphere.

C. Main Group Compounds

As discussed above, carborane derivatives as well as main group ate adducts containing heteroatom donors seldom form extended carbon contacts with higher alkali metals. Structural data on these compounds are given in Table XI.

D. Enolates

Only recently has the first X-ray structural determination of simple enolates of the heavier alkali metals been reported (Table XII) (292). As in known lithium examples, smaller aggregates are found. Sodium pinacolone enolate, $[\text{Na OC}(\text{'Bu})(=\text{CH}_2) \cdot \text{O}=\text{C}(\text{Me})(\text{'Bu})]_4$ (**64**) forms a cubic tetramer. This



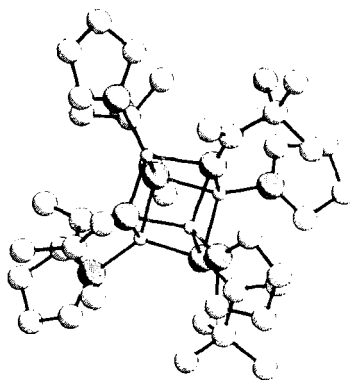
64: ligands omitted

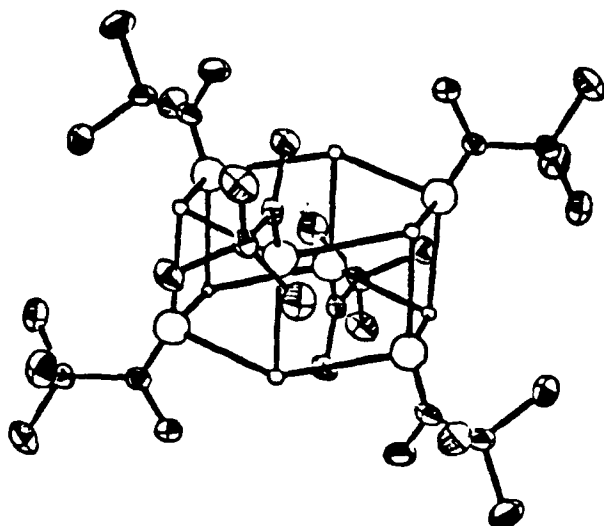
TABLE XI
 SOME STRUCTURAL DATA OF MAIN GROUP METALLATES AND RELATED SUBSTANCES

Compound	Coordination	Range (average) (Å)	Ref.
$\text{NaNO}_3 \cdot [\text{HgMe}(1\text{-Me-T})^a] \cdot (\text{H}_2\text{O})_{0.5}$	O_6	(2.35)	281
$\text{NaNO}_3 [\text{HgMe}(1\text{-Me-T})]$	O_6	Not reported	282
$[\text{Na}(\text{b-15-c-5})_2][\text{BPh}_4]$	O_{10}	2.48–3.30	283
$[\text{Na}(\text{C}_{30}\text{H}_{35}\text{O}_5\text{N})][\text{BPh}_4] \cdot \text{H}_2\text{O}$	O_6N_1	Not reported	284
$\text{NaBPh}_4[\text{VO}(\text{salen})]$	O_6	2.38	285
$\text{NaBPh}_4[\text{Co}(\text{salen})]_2 \cdot (\text{thf})_2$	O_6	2.35–2.48 (2.40)	134
$\text{NaBPh}_4[\text{Ni}(\text{salen})]_2 \cdot (\text{MeCN})_3$	O_6	2.39–2.42	286
$\text{K} [\text{B}_2(\text{H})\text{Me}_4\text{C}_8\text{H}_6] \cdot (\text{dioxane})_3$	O_4	2.72–2.81 (2.78)	287
$[\text{K}(\text{db-18-c-6})][\text{Al}_2\text{Me}_6\text{OPh}]$	O_6	2.71–2.79 (2.76)	156
$[\text{K}(\text{db-18-c-6})][\text{Al}_2\text{Me}_6\text{N}_3] \cdot (\text{C}_{11}\text{H}_9)_{1.5}$	O_6	Not reported	166
$[\text{K}(\text{db-18-c-6})][\text{AlMe}_3\text{NO}_3] \cdot (\text{C}_6\text{H}_6)_{0.5}$	O_6	2.71–2.88 (2.74)	173
$\text{K} [\text{AlCl}_3\text{Me}]$	Cl_4C_1	KC 3.21 KCl 3.27–3.58	178
$\text{K} [\text{BF}_3\text{Me}]$	F_7	KF 2.68–2.97 (2.79) KC 3.79–3.92	177
$\text{K} [\text{BF}_3\text{CF}_3]$			288
$\text{K}_2 [\text{GeF}_4(\text{CF}_3)_2]$	F_{10}	2.64–3.27	289
$\text{Cs} (\text{Me}_2\text{---C}_2\text{B}_9\text{H}_9)$	Cs-B	> 3.47	179
$\text{Cs} (p\text{-C}_6\text{H}_4\text{NCS})\text{C}_2\text{B}_9\text{H}_{10}\text{I}$	Not reported		290
$[\text{Cs}(\text{18-c-6})][\text{Al}_3\text{Me}_9\text{SO}_4]$	O_8	3.08–3.59	175
$\text{Cs} [\text{BF}_2(\text{CF}_3)_2]$	F_{12}	3.05–3.39	291

^a 1-Me-T, 1-methylthiminato.

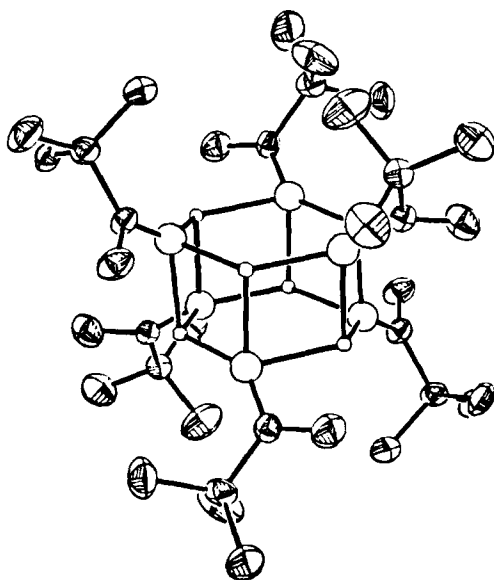
is the very same arrangement as is adopted by the THF-solvated lithium enolate, $[\text{LiOC}(\text{'Bu})(=\text{CH}_2) \cdot \text{thf}]_4$ (**65**) (293). In contrast, for the potassium compound, $[\text{K OC}(\text{'Bu})(=\text{CH}_2) \cdot \text{thf}]_6$ (**66**) (292), a hexameric aggregate has





66: ligands omitted

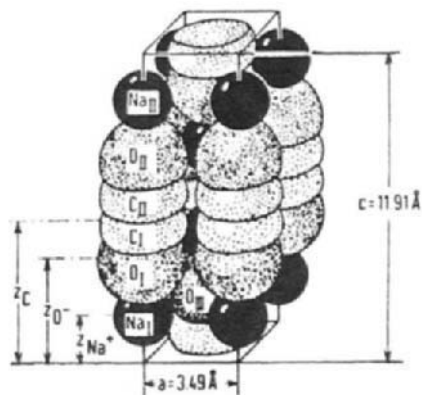
been characterized; the unsolvated $[\text{Li OC}(\text{'Bu})(=\text{CH}_2)]_6$ hexamer (67) possesses the same topology. In comparison of both aggregates, the potassium cations are displaced to the outside of the hexagonal M_6O_6 prism relative to the lithium positions.



67: ligands omitted

TABLE XII
ENOLATES AND RELATED SYSTEMS

Compound	Coordination	Range (average) (Å)	Ref.
Enolates			
$[(\text{Na OC}_6\text{H}_{11}) \cdot (\text{C}_6\text{H}_{12}\text{O})]_4$	O_4	2.24–2.33 (2.25)	292
$[(\text{K OC}_6\text{H}_{11}) \cdot (\text{thf})]_6$	O_4	2.57–2.80 (2.67)	292
Acetylenediolates			
$\text{Na}_2 \text{ OC}\equiv\text{CO}$	$\text{O}_1 + \text{O}_4$	2.20–2.42	294
$\text{K}_2 \text{ OC}\equiv\text{CO}$	$\text{O}_1 + \text{O}_4$	2.66–2.78	295
$\text{Rb}_2 \text{ OC}\equiv\text{CO}$	$\text{O}_1 + \text{O}_4$	2.82–2.92	296
$\text{Cs}_2 \text{ OC}\equiv\text{CO}$	$\text{O}_1 + \text{O}_4$	2.99–3.09	296



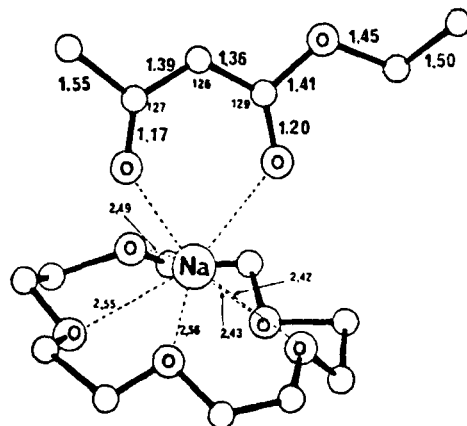
β -Diketonate Compounds

Na (acac)·H₂O

K (acac)·(H₂O)_{0.5}

Na (CH₃COCHCOPh)·(C₂H₆O₂)

Rb₂Na (hfacac)₃



Na(15-c-5)(CH₃COCHCOOEt)

K (18-c-6)(CH₃COCHCOOEt)

K (2,2,2)Li(CH₃COCHCOOEt)₂

Na(C₁₅H₁₁O₄)·2H₂O

Sodium lucidonate

O ₆	2.32–2.42 (2.38)	297
O ₇	2.65–3.05	298
O ₅	(2.33)	299
Rb-1 O ₇ F ₁	RbO 2.90–3.64	300
	RbF not reported	
Rb-2 O ₃ F ₄	RbO 2.84–2.87 (2.86)	
	RbF 2.80–3.35	
Na O ₆	NaO 2.20–2.47 (2.35)	

O ₇	2.30–2.56 (2.44)	301
O ₈	2.65–3.02 (2.92)	302
O ₆ N ₂		303
O ₆	2.32–2.77 (2.41)	304

(continued)

TABLE XII (continued)

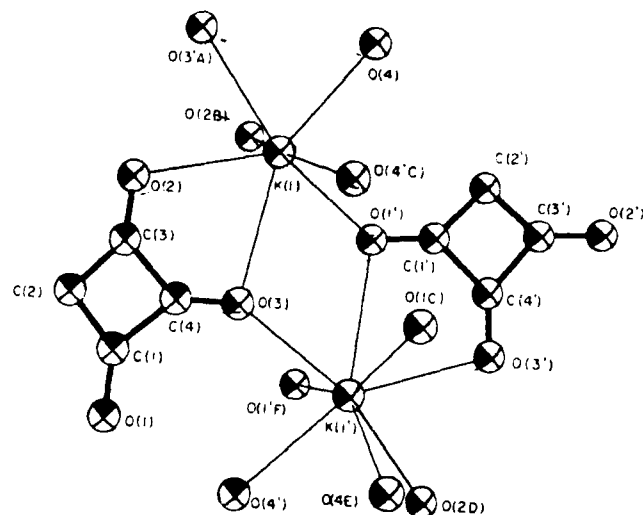
Compound	Coordination	Range (average) (Å)	Ref.
$\text{Na}(\text{C}_{21}\text{H}_{28}\text{NO}_5) \cdot (\text{H}_2\text{O})_{0.5} \cdot (\text{CH}_3\text{OH})_{0.5}$ Sodium dimethoxy(depyrrolo)dimethyl-corynantheidinate	O_5	2.26–2.47 (2.35)	305
$\text{K}_2(\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_9) \cdot (\text{H}_2\text{O})_2 \cdot (\text{CH}_3\text{OH})_2$ Dipotassium oxytetracycline	O_7	2.62–3.13 (2.83)	306
$\text{Na}(\text{C}_{41}\text{H}_{53}\text{BrN}_2\text{O}_{13})$ Antibiotic M 139603	O_6	Not reported	307
$\text{Cs}(\text{C}_{30}\text{H}_{36}\text{O}_7) \cdot 3 \text{H}_2\text{O}$ Cesium chlorothicolid methylester	O_6	(3.08)	308
$\text{Cs}(\text{C}_8\text{H}_4\text{F}_3\text{O}_2\text{S})$ Cesium 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione	O_6F_2	CsO 3.03–3.39 (3.15) CsF 3.26, 3.43	309
Enolate complexes			
K $[\text{Cd}(\text{acac})_3] \cdot \text{H}_2\text{O}$	O_6	(2.73)	310
K $[\text{Pt}(\text{acac})_2\text{Cl}]$	K-1 O_6 K-2 O_2Cl_4	(2.81) KO (2.85) KCl (3.25)	311
Cs $[\text{Eu}(\text{hfacac})_3]$	O_6F_6	CsO (3.38) CsF (3.22)	312
Cs $[\text{Am}(\text{hfacac})_3]$	O_6F_6	CsO (3.35) CsF (3.27)	312
Cs $[\text{Y}(\text{hfacac})_4]$	F_8	3.21–3.75	313
$[\text{NaOEt} \cdot \text{Fe}(\text{acacen}) \cdot \text{thf}]_2$	O_4	2.24–2.37 (2.33)	314
K $[\text{Co}(\text{acacen})(\text{gly})_2]$	O_5	(2.77)	315
$\text{K}_2 [\text{PdCl}_2(\text{C}_6\text{O}_4\text{Cl}_2)] \cdot (\text{H}_2\text{O})_4$	O_6	2.72–2.83 (2.79)	316
$\text{K}_2 [\text{PdCl}_2(\text{C}_6\text{O}_4\text{Cl}_2)] \cdot (\text{H}_2\text{O})_4$	O_6	2.72–2.91 (2.82)	316

Square acids, croconates, tropolanates, and related compounds

K (C₄H₁O₃)·H₂O

O₇ 2.72–2.99 (2.84)
O₈ 2.76–3.17 (2.91)

317



K (C₄H₁O₃)·H₂O

K₂ (C₄O₄)·H₂O

Rb (C₅H₁O₅) Rubidium hydrogen croconate

K₂ (C₁₁N₄O₃)·(H₂O)₂

Dipotassium bis(dicyanomethylene)croconate

O₅ 2.73–2.95 (2.85)
Not reported
O₇ 2.81–3.04 (2.94)

318

319

320

321

N₄O₆ KN 3.00–3.29 (3.12)
KO 2.80–2.94 (2.88)
N₄O₅ KN 2.93–3.15 (3.02)
KO 2.66–2.89 (2.80)

(continued)

TABLE XII (continued)

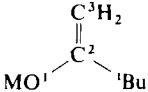
Compound	Coordination	Range (average) (Å)	Ref.
Na (C ₇ H ₅ O ₂) Sodium tropolonate	O ₆	2.37–2.60	322
K ₂ (C ₆ H ₂ O ₄) Dipotassium 2,5-dihydroxy-1,4-benzoquinone	O ₆	2.7–3.0	323
Na ₂ (C ₈ N ₈)·(H ₂ O) ₄ Disodium [3,4-bis(cyanimino)]-1-cyclobutene-1,2-diyl(cyanamidate) tetrahydrate	O ₃ N ₃	NaO 2.34–2.41 (2.39) NaN 2.50–2.58 (2.53)	324
Rb ₂ (C ₄ N ₂ S ₂)·H ₂ O Dirubidium <i>cis</i> -1,2-dicyanoethylene-1,2-dithiolate	2 ₆ N ₂	RbS 3.46–3.64 (3.58) RbN 3.09	325
	S ₂ N ₂ O ₃	RbS 3.61 RbN 3.02 RbO 2.98–3.21	
K ₂ (C ₄ S ₄)·H ₂ O Dipotassium tetrathiosquarate	S ₇ O ₁	KO (2.91) KS 3.58	326
K ₂ [Ni(C ₄ O ₂ S ₂) ₂]·(H ₂ O) ₂ Dithiosquarate nickelate	O ₆	(2.84)	327
K {Cu[C ₂ S ₂ (COOEt) ₂] ₂ }·Et ₂ O	O ₅	(2.67)	328
Na·(Me ₃ NCH ₂ Ph) ₂ [Cu ₃ (SCH=CHS) ₃]·MeOH		NaO 2.32 NaS 2.78–2.82 (2.80)	327a
Potassium bis(1,2-dicarboxyethoxy-ethene-1,2-dithiolato)cuprate			

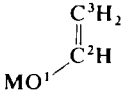
Within the set of alkali pinacolonates, increasing cation size and decreasing degree of solvation favors higher aggregation. A comparison of bonding geometries (Table XIII) in these alkali enolate structures with those obtained by *ab initio* calculations (33) illustrates the countercation dependence due to charge localization on the oxygens.

Beside these simple enolates, quite a few enolized β -diketo structures have been reported. Similarly, much work has been done on troponolates, squarates, and croconates. Acetylenediolates, which are synthesized by reduction of carbon monoxide, may be regarded as enolate derivatives as well. As expected, only oxygen coordination is observed for the compounds summarized in Table XII. Some related sulfur derivatives are also listed.

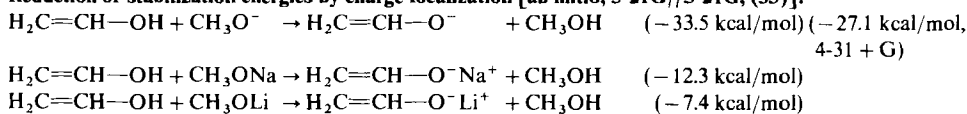
TABLE XIII

CHARGE LOCALIZATION BY ALKALI COUNTERCATIONS: SELECTED GEOMETRIC AND ENERGETIC PARAMETERS OF ENOLATE ANIONS. EXPERIMENTAL AND THEORETICAL COMPARISON

Experimental					
					
M	Compound	$d(\text{O}-1-\text{C}-2)^a$	$d(\text{C}-2=\text{C}-3)^a$	$\Delta \text{O}-1-\text{C}-2=\text{C}-3$	Ref.
Li	65	1.35	1.34	—	293
Li	67	1.342	1.330	121.8	292
Na	64	1.308	1.358	122.8	292
K	66	1.306	1.350	122.1	292

Ab initio (3-21G//3-21G) (33):			
			
M	$d(\text{O}-1-\text{C}-2)^a$	$d(\text{C}-2=\text{C}-3)^a$	$\Delta \text{O}-1-\text{C}-2=\text{C}-3$
H	1.371	1.315	127.2 (cis), 121.9 (trans)
Li	1.321	1.325	127.0
Na	1.317	1.332	128.2
free anion	1.269	1.365	129.7 (4-31 + G)

Reduction of stabilization energies by charge localization [ab initio, 3-21G//3-21G, (33)]:



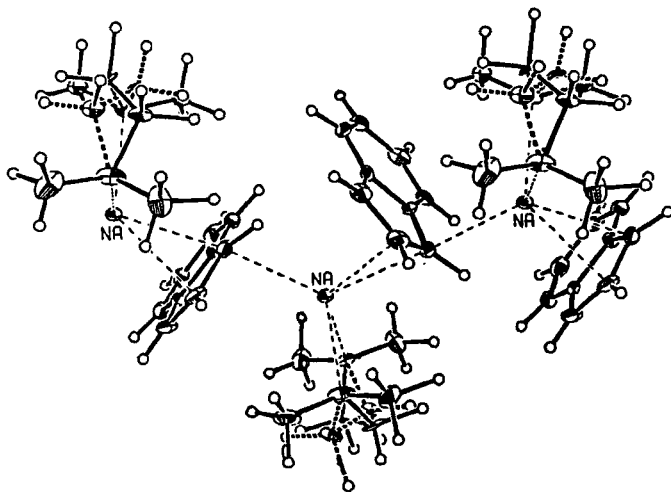
^a Angstroms.

Additional structures can be regarded as enolates: phenolates, barbiturates, hydroxythiadiazines, etc. Many other substances like nitroso compounds, triazoles, xanthines, or glyoximatochelates, e.g., may involve resonance structures, with a negative charge on a conjugated carbon atom. However, these compounds are of limited interest from the organometallic viewpoint of this article and are not discussed here.

VI

ADDENDUM

In the meantime, some additional organoalkali structures have come to our attention. (1) Indenylsodium·tmeda (**68**) (329) crystallizes in an infinitely aggregated chain structure. The smaller Li cation in indenyllithium·tmeda (330) prefers an ion pair structure in contrast. Sodium cations bridge two indenyl units in **68**. They are bonded η^1 to a benzylic C(7) site [$d(\text{C}-\text{Na}) = 2.58 \text{ \AA}$] of one and bridge the C(7') and C(8') site of the other hydrocarbon moiety [$d(\text{C}-\text{Na}) = 2.67, 2.69 \text{ \AA}$, η^2]. The zigzag arrangement is in close analogy to that of Na cp·tmeda (**13**), while the indenyl-sodium bonding resembles that in benzylnsodium·tmeda (**8**). (2) $[\text{K}(\text{diglyme})]_2[\text{Yb}(\text{C}_8\text{H}_7\text{-tBu})_2]$ is another example of η^8 -coordination of potassium ions to cyclo-octadienyl systems (331). The structure closely resembles that of the triple ion pair $[\text{K}(\text{dme})]_2\text{-}[\text{Yb}(\text{COT})_2]$ (**22**). (3) $[\text{Na}(\text{p-tert-butylmethoxycalix-[4]arene})][\text{Me}_3\text{AlO-(AlMe}_2)_2\text{OOCPh}]\cdot(\text{toluene})$ is built up by calixarene



coordinated sodium cations (332). The fifth coordination site is occupied by a methyl group of the aluminate anion. The Na—C distance (2.64 Å) is as short as that in ethyl-sodium (3). (4) In a reaction product of Na cp with SbCl_3 , $[\text{Na}(\text{thf})_3][\text{Sb}_4(\mu_3\text{-C}_5\text{H}_3)_3(\mu_2\text{-C}_5\text{H}_3)(\eta^1\text{-C}_5\text{H}_5)]$, the THF-solvated sodium cation is bound η^5 to the μ_2 -cyclopentadienyl moiety at carbon–metal distances of 2.70–2.84 Å (2.78 Å, average) (333). (5) The crystal structure of $\text{K C}_5\text{H}_4\text{SiMe}_3$ consists of infinite, zigzag-puckered chains of potassium ions, which are intersected by pentahapto-bound cyclopenta-dienyl moieties (334). The potassium ions bind η^2 to a cyclopentadienyl unit of a neighboring string in addition [$d(\text{C}—\text{K}) = 2.99\text{--}3.08$ Å, η^5 ; $3.67\text{--}3.68$ Å, η^2]. The structure resembles that of Na cp·tmeda (13) and of Tl cp (335) closely. (6) In two zeolithe sorption complexes, K zeolithe-L·(pyridine)_x (336) and Na zeolithe-L·(benzene)_x (337), η^6 attachment of the aromatic π system to alkali sites of the aluminosilicate framework has been observed.

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1. The section on General Aspects presents reviews on the general organometallic chemistry of the heavier alkali metals.
2. Periodic Reviews gives references to the latest annual surveys of alkali metal chemistry. Inorganic periodicals often include organometallic topics as well.
3. Selected Compounds deals with properties of selected classes of alkali organometallic compounds: radical anions, transition metal derivatives, ate complexes, and graphite intercalates.
4. Selected Properties summarizes work on mechanistic, solution NMR, and theoretical investigations of alkali metal derivatives.
5. Publications, which refer mainly to Synthetic Applications of organometallic compounds, are presented in the next section.
6. Organometallic compounds which do not involve carbon-metal contacts (enolates, alkoxides, alkylamides, electrides, carbonyl compounds, carboxylates) are quoted by Related Compounds references.
7. Publications which aim at Crown Ether and Polyamine Chelated Compounds are presented in the last section.

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Trimethylenemethane Metal Complexes

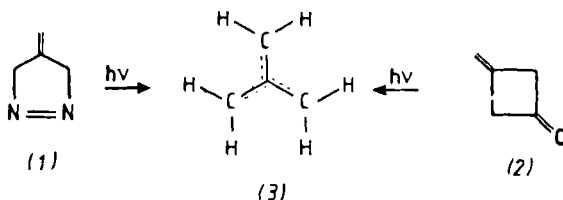
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I

INTRODUCTION

Low-temperature matrix photolysis of 4,5-dihydro-4-methylene-3H-pyrazole (**1**) or 3-methylenecyclobutanone (**2**) generates the short-lived and highly reactive triplet diradical trimethylenemethane (**3**) which is stable only at -185°C (*1-4*). The existence of **3** as a ground-state triplet was confirmed by ESR spectroscopy (*1*), and in 1966 Emerson *et al.* reported the first trimethylenemethane metal complex, $[\text{Fe}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_3]$ (**4**), which is stable and easily handled at room temperature (*5*). The availability of 2-[(trimethylsilyl)methyl]allyl esters and halides, which serve as trimethylenemethane equivalents, has renewed the interest in trimethylenemethane metal complexes and their role in catalytic synthesis of cyclopentanoids (*6,7*). In this article we discuss these developments and provide an up-to-date review of trimethylenemethane metal complexes. Previous reviews are now somewhat dated (*4,8*).

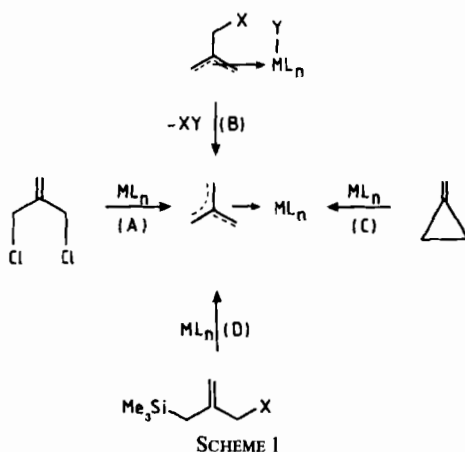


II

SYNTHESIS OF TRIMETHYLENEMETHANE METAL COMPLEXES

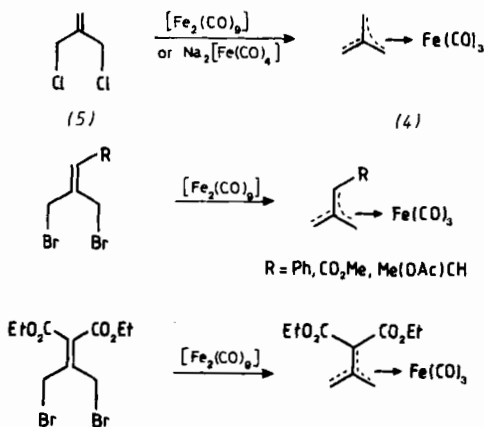
Trimethylenemethane metal complexes have been synthesized via four main routes: (A) the dehalogenation of α, α' -dihalosubstituted precursors, (B) the thermal extrusion of XY (XY = HCl, Br₂, and CH₄) from η^3 -methylallyl complexes, (C) the ring opening of alkylidenecyclopropanes, and (D) the

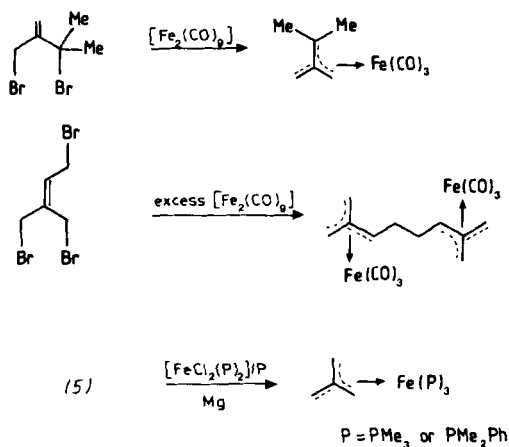
elimination of Me_3SiX [$\text{X} = \text{OAc}, \text{Cl}, \text{OS}(\text{O})_2\text{Me}$] from functionalized allyl silanes (Scheme 1).



A. Dehalogenation of α, α' -Dihalosubstituted Precursors

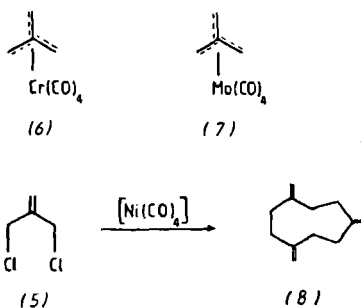
Tris(carbonyl)- η^4 -trimethylenemethaneiron(0) (4) was the first trimethylenemethane metal complex to be synthesized and was obtained from the reaction of 3-chloro-2-chloromethylprop-1-ene (5) with $[\text{Fe}_2(\text{CO})_9]$ or $\text{Na}_2[\text{Fe}(\text{CO})_4]$ (5,9,10). A number of substituted trimethylenemethane iron complexes have been prepared by similar methods to those used to prepare 4, and the results are summarized in Scheme 2 (9,11,12).



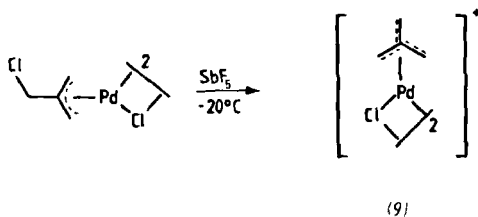


SCHEME 2 (continued)

Treatment of 3-chloro-2-chloromethylprop-1-ene (5) with $[\text{Cr}(\text{CO})_6]$ or $[\text{Mo}(\text{CO})_5]^{2-}$ afforded low yields of the trimethylenemethane complexes 6 and 7, respectively (10). Interestingly, treatment of 5 with the d^{10} complex $[\text{Ni}(\text{CO})_4]$ gave the hydrocarbon 8 and not a stable nickel trimethylenemethane complex (13).



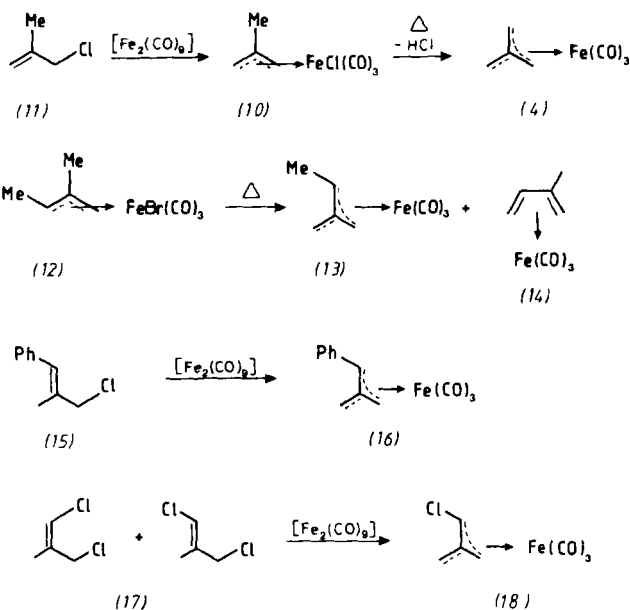
A trimethylenemethane complex of palladium(II) (9), which has not been isolated, is reported to be formed in solution on treatment of $[\text{Pd}_2\text{Cl}_2\{\eta^3\text{-CH}_2\text{C}(\text{CH}_2\text{Cl})\text{CH}_2\}_2]$ with SbF_5 (14). The reaction of the allyl chloride 5



with $[\text{Fe}_2(\text{CO})_9]$ is promoted by ultrasound to afford the trimethylenemethane complex **4** in quantitative yield (15). The use of ultrasonics in promoting reactions may find applications in the synthesis of various substituted trimethylenemethane complexes.

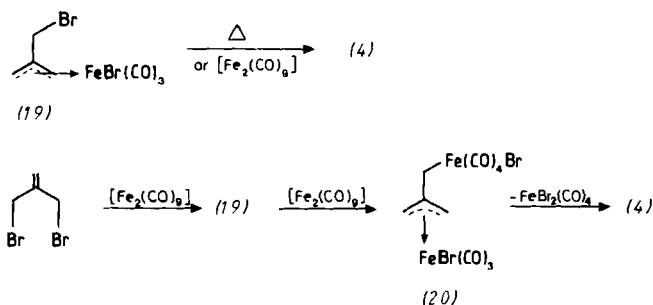
B. Thermal Extrusion from η^3 Allyl Complexes

The thermal extrusion of a simple molecule from an η^3 -allyl complex, to generate an η^4 -trimethylenemethane metal complex, was originally observed by Emerson. The iron allyl complex **10**, obtained from the reaction of 3-chloro-2-methylprop-1-ene (**11**) with $[\text{Fe}_2(\text{CO})_9]$, decomposed on heating to afford the iron trimethylenemethane complex **4** (9,16). Similarly, the decomposition of the allyl complex bromotris(carbonyl)-1,2-dimethylallyliron(II) (**12**) gave a mixture of the methyltrimethylenemethane complex **13** and tris(carbonyl)isopreneiron(0) (**14**) (9). In certain cases the intermediate η^3 -methylallyl complex could not be isolated. Thus 2-chloromethyl-1-phenylprop-1-ene (**15**) reacts with $[\text{Fe}_2(\text{CO})_9]$ to give the η^4 -trimethylenemethane complex **16**, and similarly a mixture of *cis*- and *trans*-1,3-dichloro-2-methylprop-1-ene (**17**) reacted with $[\text{Fe}_2(\text{CO})_9]$ to give complex **18** (9).



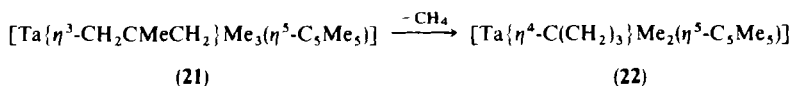
A similar elimination process was observed for the complex, bromotris(carbonyl)-2-bromomethylallyliron(II) (**19**), which afforded the iron

trimethylenemethane complex **4** via a thermal reaction or in the presence of $[\text{Fe}_2(\text{CO})_9]$ (9). This reaction is of interest because, although the mechanism for the dehalogenation of 2-halomethyl-3-halopropan-1-ene by $[\text{Fe}_2(\text{CO})_9]$ has not been rigorously determined, it probably involves the elimination of $[\text{FeBr}_2(\text{CO})_4]$ from an η^3 -allyl intermediate (**20**) and can be viewed as a thermal extrusion type reaction (Scheme 3) (9). Another example of a thermal



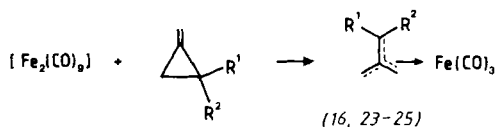
SCHEME 3

elimination reaction was observed for the η^3 -2-methylallyl tantalum complex **21**, obtained from the reaction of $[\text{TaClMe}_3(\eta^5\text{-C}_5\text{Me}_5)]$ with methylallyl magnesium chloride, which eliminates methane at ambient temperatures to afford the trimethylenemethane complex **22** (17).



C. Ring Opening of Alkylidenecyclopropanes

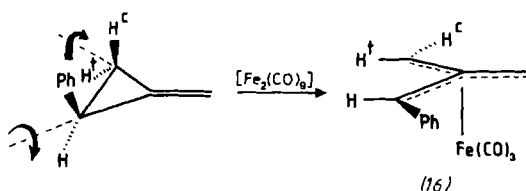
The ring opening of 2-substituted methylenecyclopropanes in the presence of $[\text{Fe}_2(\text{CO})_9]$ afforded the η^4 -trimethylenemethane complexes **16** ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Ph}$), **23** ($\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Ph}$), **24** ($\text{R}^1 = \text{R}^2 = \text{Ph}$), and **25** ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CH}=\text{CH}_2$) (see Scheme 4) (18,19). The stereochemistry of the ring



SCHEME 4

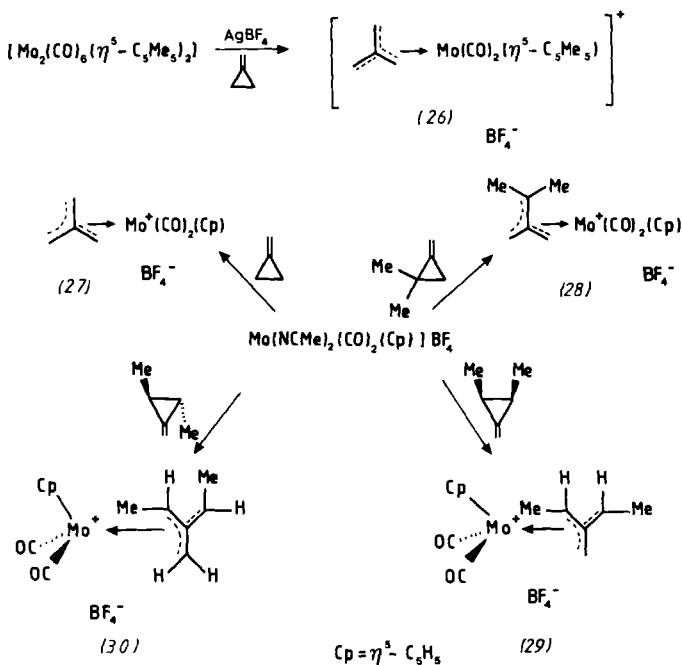
opening of 2-phenylmethylenecyclopropane to give the (η^4 -phenyltrimethylenemethane)iron complex (**16**) has been elucidated by stereospecific deuterium labeling experiments and shows that a specific disrotatory mode

of ring opening occurs, as predicted by frontier molecular orbital diagrams (Scheme 5) (20-23).



SCHEME 5

The reaction of $[\text{Mo}_2(\text{CO})_6(\eta^5\text{-C}_5\text{Me}_5)_2]$ with methylenecyclopropane and AgBF_4 afforded the cationic trimethylenemethane complex **26** (24). Methylene-cyclopropane and 2,2-dimethylenecyclopropane also ring open in the presence of $[\text{Mo}(\text{NCMe})_2(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]\text{BF}_4$ to give the cationic trimethylenemethane complexes **27** and **28**, respectively. The mode of ring opening was verified by the use of *cis*- and *trans*-2,3-dimethylmethylene-cyclopropane to afford, respectively, the *syn,syn*- and the *syn,anti*-dimethyl-trimethylenemethane complexes **29** and **30**, which are consistent with a disrotatory-out ring opening reaction where the breaking 2,3- σ bond bends away from the metal (Scheme 6) (24,25). However, reactions of methylene-

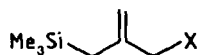


SCHEME 6

cyclopropanes with low-valent metal complexes do not always afford trimethylenemethane metal complexes (26–34). We also note that methylenecyclopropanes are ring opened by zero-valent nickel and palladium, but whether these reactions involve trimethylenemethane intermediates is not clear (35).

D. Elimination of Me₃SiX [X = OAc, Cl, OS(O)₂Me] from Functionalized Allyl Silanes

The ability of [Pd(PPh₃)₄] to promote the elimination of trimethylsilyl acetate from the allyl silane **31a** and generate a highly reactive η^3 -trimethylenemethane palladium intermediate which is considered to be of the form [Pd{ η^3 -C(CH₂)₃}(PPh₃)₂], was first observed by Trost and Chan (6,7).



- 31** a, X = OAc
 b, X = OS(O)₂Me
 c, X = Cl

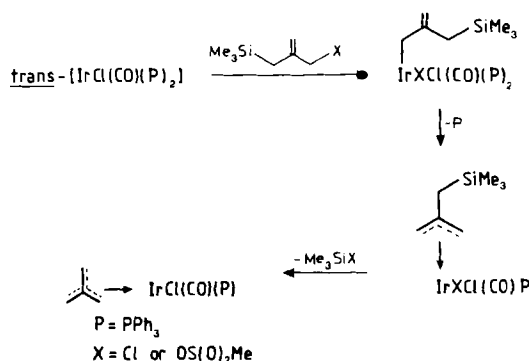
Using this methodology, we have developed a high-yield route to a variety of air-stable trimethylenemethane metal complexes of iridium, rhodium, osmium, and ruthenium by reaction of the allyl silane **31b** with suitable low-valent *d*⁸ metal precursors (Table I) (36,37). The success of this route appears to be related to the ability of allylic methanesulfonates to rapidly oxidatively

TABLE I
 FORMATION OF TRIMETHYLENEMETHANE METAL COMPLEXES FROM ALLYL SILANES^a

Substrate	Reagent	Product	Yield (%)
[IrCl(CO)P ₂]	31c	[IrCl(CO)P(tmm)]	11
[IrCl(CO)P ₂]	31b	[IrCl(CO)P(tmm)]	75
[IrBr(CO)P ₂]	31b	[IrBr(CO)P(tmm)]	76
[IrCl(CO)As ₂]	31b	[IrCl(CO)As(tmm)]	77
[IrCl(CO)P ₂]/KPF ₆	31c	[Ir(CO)P ₂ (tmm)]X	60
[IrH(CO)P ₃]	31b	[Ir(CO)P ₂ (tmm)]Y	90
{Ir ₂ Cl ₂ (C ₈ H ₁₄) ₄ }/4P	31b	[IrClP ₂ (tmm)]	45
[RhClP ₃]	31b	[RhClP ₂ (tmm)]	50
[Os(CO) ₂ P ₃]	31a	[Os(CO) ₂ P(tmm)]	11
[Os(CO) ₂ P ₃]	31b	[Os(CO) ₂ P(tmm)]	35
[OsCl(NO)P ₃]	31b	[OsCl(NO)P(tmm)]	20
[RuCl(NO)P ₂]	31b	[RuCl(NO)P(tmm)]	20

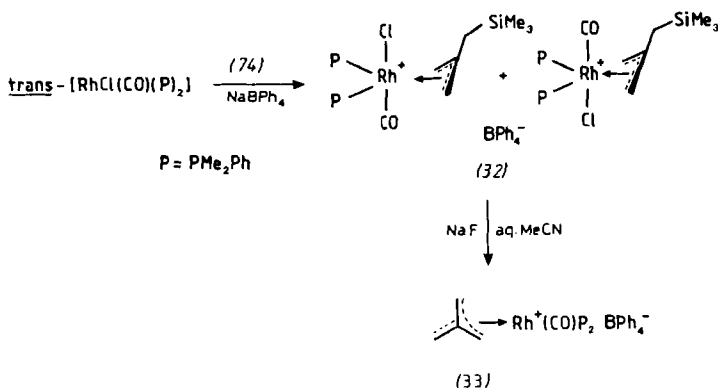
^a X = PF₆, Y = OS(O)₂Me, P = PPh₃, As = AsPh₃, tmm = η^4 -trimethylenemethane.

add to low-valent metal centers coupled with the poor coordinating ability of the methanesulfonate group (38). Release of methanesulfonate from the metal center followed by desilylation of the η^3 -trimethylsilylmethylallyl intermediate is considered to be a key step in the mechanism of formation of the trimethylenemethane metal complex (Scheme 7). Thus while palladium(0) promotes the ionization of allyl acetates (39) this is not necessarily the case with other metal centers, and studies to date show that the acetate **31a** is in general a poor precursor to trimethylenemethane complexes (40).



SCHEME 7

The reactions of the allylsilanes **31** with a d^8 metal center is believed to proceed via oxidative addition to the metal to give an η^1 -allyl, formation of an η^3 -allyl, and elimination of Me_3SiX to afford the η^4 -trimethylenemethane complex (Scheme 7). The isolation of the allylic complex **32** from the reaction of $\text{trans-}[\text{RhCl}(\text{CO})(\text{PMe}_2\text{Ph})_2]$ with **31b** in the presence of NaBPh_4 provides

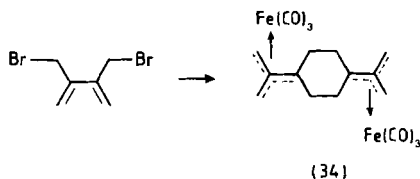
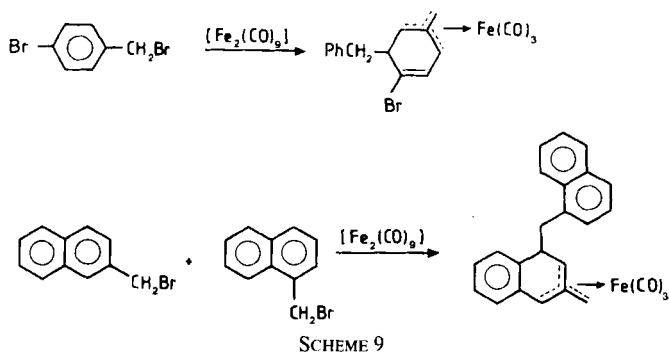


SCHEME 8

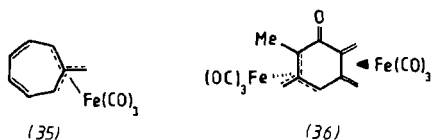
evidence for this mechanism. Addition of sodium fluoride to **32** afforded the trimethylenemethane complex **33** in quantitative yield (Scheme 8) (37).

E. Other Routes

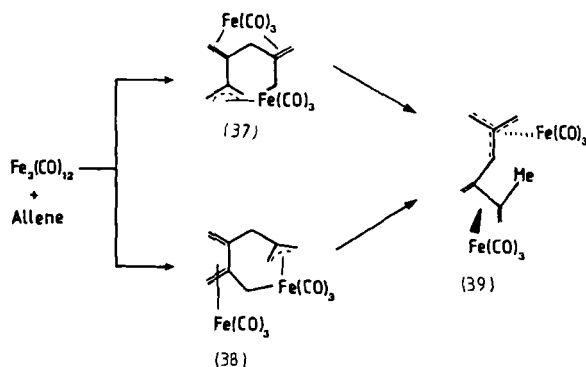
A variety of trimethylenemethane iron complexes have been obtained by reactions of certain bromomethylaryl compounds with $[\text{Fe}_2(\text{CO})_9]$, and the results are summarized in Scheme 9 (41–43). A similar C—C coupling of 2,3-dibromomethylbutadiene gave the complex **34**, isolated as *cis* and *trans* isomers in 7.5 and 2% yields, respectively (44,45).



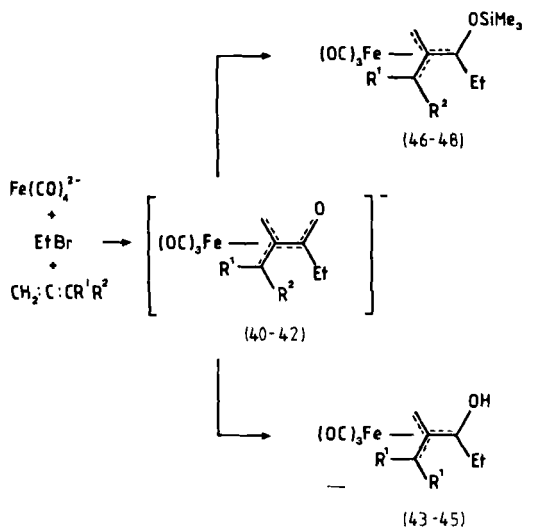
A number of iron trimethylenemethane complexes can also be obtained via other routes. Thus $[\text{Fe}_2(\text{CO})_9]$ reacts with 7-(hydroxymethyl)cycloheptatriene to afford the complex **35** (46,47), while 2,3,5,6-tetramethylene-7-oxa-bicyclo[2.2.1]heptane with $[\text{Fe}_2(\text{CO})_9]$ gave the complex **36** in low



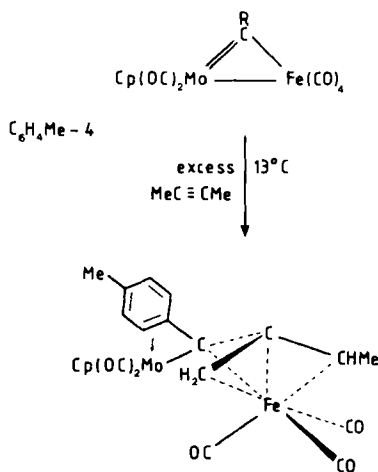
yield (48). Interestingly, the reaction of allene with $[\text{Fe}_2(\text{CO})_9]$ gave the complexes **37** and **38** which on refluxing in toluene rearranged to the complex



39 (49). Substituted allenes react with $[\text{Fe}(\text{CO})_4]^{2-}$ and bromoethane to afford the anionic complexes **40** ($\text{R}^1 = \text{R}^2 = \text{H}$), **41** ($\text{R}^1 = \text{R}^2 = \text{Me}$), and **42** ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Ph}$), which on protonation gave the complexes **43–45**, respectively, or on treatment with chlorotrimethylsilane yielded the complexes **46–48**. A similar reaction was observed between $[\text{Fe}(\text{CO})_4]^{2-}$ and di(bromomethyl)allene (50,51).



A novel metal-substituted trimethylenemethane complex of iron has been obtained in high yield by the action of excess but-2-yne on a dinuclear μ -alkylidyne complex (Scheme 10) (52). The structure of this complex has been substantiated by a single crystal X-ray study.



SCHEME 10

III

STRUCTURE AND BONDING

A gas phase electron diffraction study of tris(carbonyl)- η^4 -trimethylenemethaneiron (**4**) establishes that the carbonyl ligands and a trigonal-pyramidal trimethylenemethane ligand are in a staggered conformation about the iron (Fig. 1), with the central carbon being closer to the iron center than the outer methylene carbons. Thus the $\text{Fe}-\text{C}(\text{central})$ distance is $1.94(1) \text{ \AA}$ while the $\text{Fe}-\text{CH}_2$ distances are 2.12 \AA (53). Single-crystal X-ray diffraction studies for a number of other iron trimethylenemethane complexes establish a similar arrangement of ligands about the metal (12,41,48, 54–58). The vibrational spectrum of **4** has been analyzed and an approximate valence force field has been calculated which reproduces the observed spectrum and indicates that there is a significant interaction between the iron and the methylene carbon atoms of the trimethylenemethane ligand (59,60). A study of the electronic structure of **4** by computer simulation also indicates that the methylene carbons are more strongly bonded to the iron than the central carbon (61), and ESCA and photoelectron spectra of **4** show that the overall donor–acceptor character of trimethylenemethane is similar to that of cyclobutadiene (62,63).

X-Ray diffraction studies on the complexes $[\text{Mo}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_2(\eta^5\text{-C}_5\text{Me}_5)]\text{BF}_4$ (25) and $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{Cl}(\text{CO})(\text{PPh}_3)]$ (40) show that the

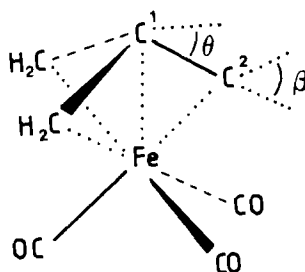


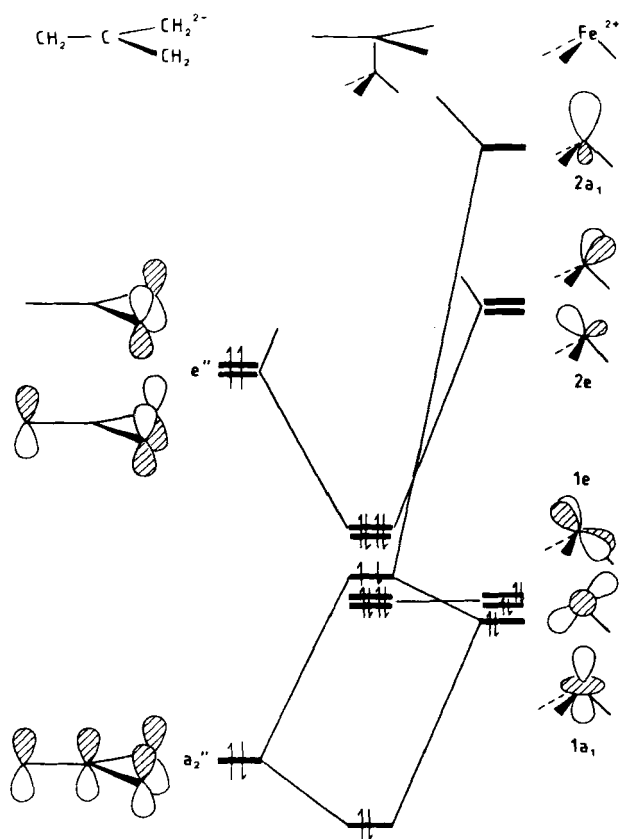
FIG. 1.

trimethylenemethane fragment again adopts the usual umbrella-type arrangement. It is interesting to note that the trimethylenemethane ligand in the iridium complex is not symmetrically bound to the metal, the Ir—CH₂ distances reflecting the markedly differing trans influences of chloride, carbon monoxide, and triphenylphosphine ligands.

The conformational preference and magnitude of rotational barriers for trimethylenemethane—ML₃ complexes have been analyzed (64,65). The orbital interaction diagram given in Scheme 11 for a planar trimethylenemethane ligand and an Fe(CO)₃ fragment in a staggered geometry shows that the primary bonding interaction in the complex is between the 2e set of the Fe(CO)₃ fragment and e'' on the trimethylenemethane ligand. On rotation about the metal—trimethylenemethane axis by 60° into an eclipsed geometry the interaction between 2e and e'' is decreased; the energy of the HOMO in the complex increases, however, and this is the main factor which provides a barrier to rotation (Fig. 2) (64,65).

Extended Hückel calculations give a barrier of 87 kJ mol⁻¹ using a planar trimethylenemethane ligand (64). Puckering the trimethylenemethane to the experimental geometry causes the calculated barrier to rise to 98.6 kJ mol⁻¹. This puckering allows mixing of s character into e'' so that these orbitals become directed more toward the metal, resulting in a greater overlap between e'' and 2e. The puckering of the trimethylenemethane ligand is quantified by θ and is in the range of 12° (25,53,55,57,66). The mixing of s character into e'' also results in the H—C—H plane being tipped away from the metal. The angle β , between C-1—C-2 and the plane H—C—H, is typically about 15° (53,55,57).

¹H- and ¹³C-NMR spectroscopy allows a convenient method of characterizing trimethylenemethane metal complexes. Rotational barriers can also be determined from variable temperature NMR studies. The ¹³C chemical shift for the central carbon atom lie in the narrow range of 104–118 ppm; the methylene carbons are more dependent on the other ligands present in the complex, and shifts of 34–90 ppm are observed (5,22,25,37). These results



SCHEME 11

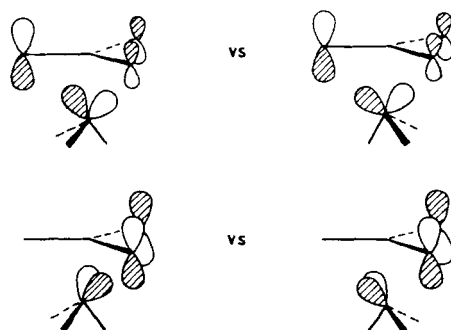


FIG. 2.

provide further evidence for a very weak interaction between the central carbon and the metal. The ^1H -NMR spectra of the complexes $[\text{M}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{L})_3]$, measured at room temperature, exhibit the characteristic features for a static trimethylenemethane ligand. Thus for $[\text{Os}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_2(\text{PPh}_3)]$ (37,40) the ^1H -NMR spectrum consists of three resonances for the trimethylenemethane ligand, consistent with the symmetry of the complex. There is a long-range "W-coupling" between H^1 and H^3 along with an additional coupling to the coordinated tertiary phosphine (Fig. 3).

No sign of rotation of the trimethylenemethane fragment could be detected at 140°C , setting a lower limit to the rotational energy barrier at 95 kJ mol^{-1} (40). However, coalescence temperatures for some iron complexes have been observed. Thus the derivatives $[\text{Fe}\{\eta^4\text{-C}(\text{CH}_2)_2(\text{CHR})\}(\text{CO})_3]$ ($\text{R} = \text{MeCO}$, MeCHOH , Et , and MeCOCHMe) exhibit three ^{13}C signals for the non-equivalent carbon monoxide ligands at room temperature. Coalescence of these resonances was observed at higher temperatures, setting the rotational barrier at $71\text{--}84\text{ kJ mol}^{-1}$ (67). Three separate ^1H -NMR signals were also found for the complex $[\text{Fe}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_2\text{PF}_3]$ at room temperature, the coalescence temperature again indicating a high rotational barrier (68). In contrast with these observations, the molybdenum complex $[\text{Mo}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]\text{BF}_4$ appears to have a very low rotational barrier since the static structure was only observed at -90°C (25). The estimated barrier to apparent rotation afforded a value of 41.4 kJ mol^{-1} . A calculated barrier for this complex gave a value of 202.7 kJ mol^{-1} , and it would appear that a dynamic process other than a simple rotation was responsible for the room temperature ^1H equivalence of the η^4 -trimethylenemethane protons. A mechanism involving slipping from an η^4 -arrangement to an η^1 -trimethylenemethane intermediate has been proposed to account for these observations.

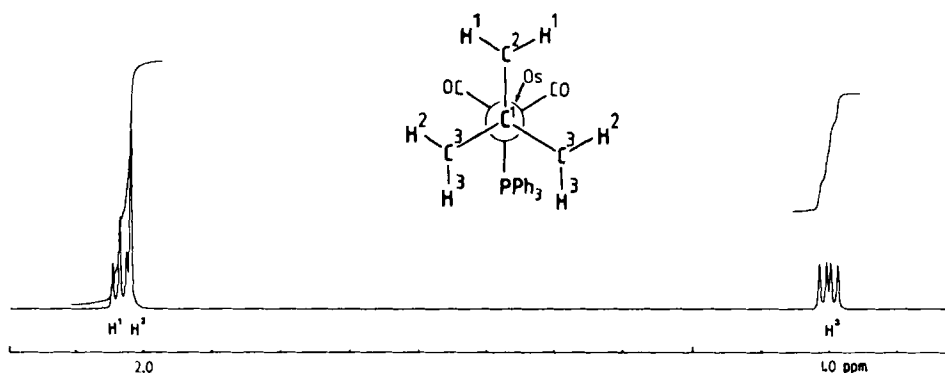
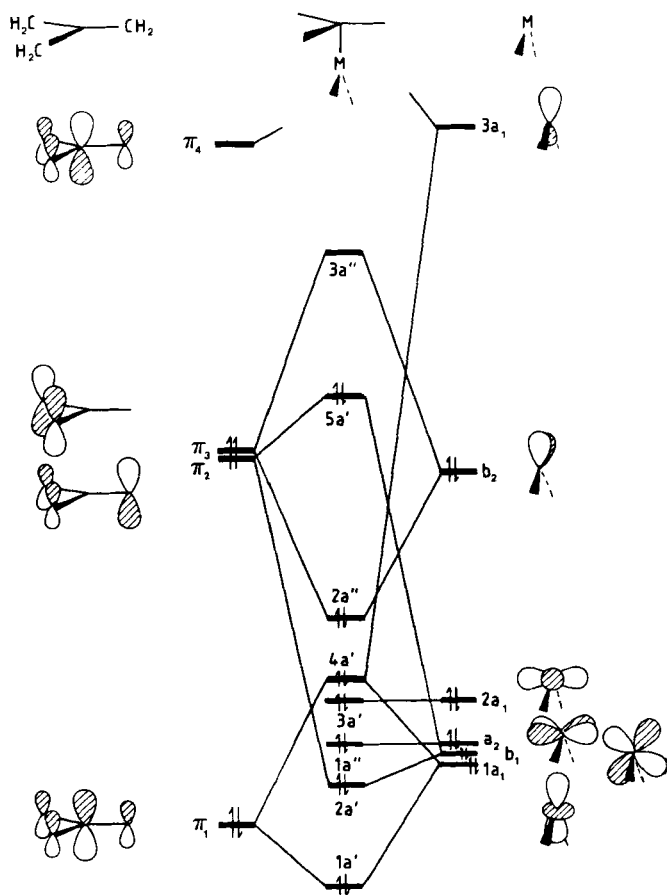


FIG. 3.

Although no stable complexes containing trimethylenemethane coordinated to a d^{10} ML_2 fragment have been isolated, the structure of such complexes have been extensively studied (69–71) due to their postulated existence in the metal-catalyzed cycloaddition of trimethylenemethane to alkenes (see Section V). Orbital interaction diagrams indicate that the preferred structure is one in which the trimethylenemethane is coordinated to the metal in an allylic fashion. The principal bonding interaction is between an orbital b_2 which is hybridized toward π_3 of the trimethylenemethane fragment (Scheme 12). The rotational barrier about the trimethylenemethane– ML_2 axis will be essentially zero. On rotation b_2 will interact with π_2 , and since π_2 and π_3 are degenerate b_2 will interact to exactly the same extent with each (Fig. 4). Albright (69) calculated that the dihedral angle between the P—M—P and



SCHEME 12

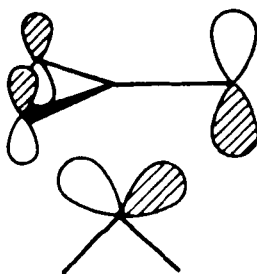


FIG. 4.

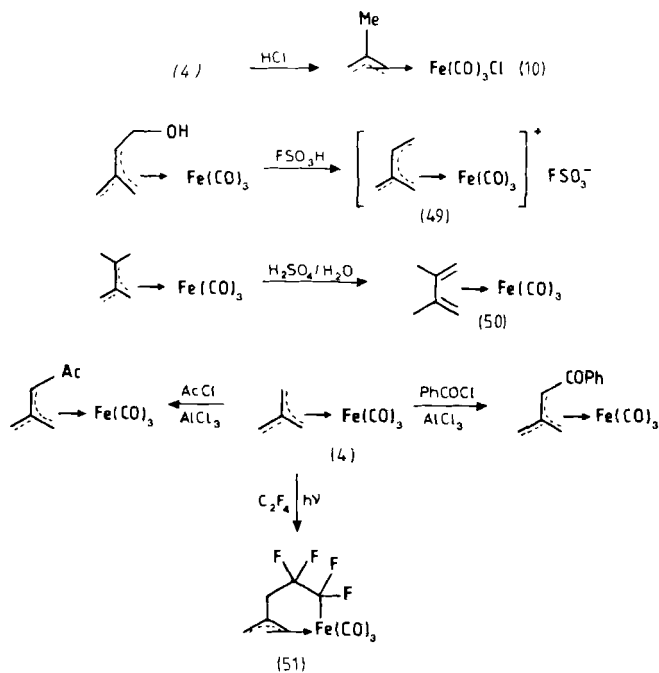
trimethylenemethane planes is 90° , but Fenske–Hall calculations (71) indicate that a dihedral angle of 96° is the favored geometry. Interestingly these calculations are constrained to a planar trimethylenemethane ligand. We have previously noted that in the related complex $[\text{Pt}\{\eta^3\text{-CH}_2\text{COCH}_2\}(\text{PPh}_3)_2]$ the dihedral angle is 128° and the C—O bond is inclined by 17° out of the C—C—C plane toward the metal (66). Similar distortions of substituents on the central carbon of η^3 -allyl complexes have been observed (72), and so it would seem likely that in the intermediates $[\text{M}\{\eta^3\text{-C}(\text{CH}_2)_3\}(\text{L})_2]$ similar distortion of the trimethylenemethane ligand would be expected.

IV

REACTIONS OF η^4 -TRIMETHYLENEMETHANE COMPLEXES

A. With Electrophiles

Initial studies have shown that iron trimethylenemethane complexes are susceptible to electrophilic attack. Thus addition of hydrochloric acid to tris(carbonyl)- η^4 -trimethylenemethaneiron (**4**) gives chlorotris(carbonyl)-2-methylallyliron(II) (**10**) (9), while substituted trimethylenemethane iron complexes react with strong acids to afford cross-conjugated dienyl iron cations (**49**) and η^4 -diene complexes (**50**) (9,11,73). The complex bromotris(carbonyl)-2-bromomethylallyliron (II) (**19**) is obtained from the reaction of bromine with **4** (9), and Friedel–Crafts acylation of the trimethylenemethane ligand of complex **4** is also possible (9). Photolysis of **4** in the presence of tetrafluoroethylene affords an η^3 -allyl complex (**51**) where addition across the metal and the trimethylenemethane ligand occurs (74). The complex $[\text{Os}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_2\text{PPh}_3]$ reacts rapidly with hydrochloric acid to yield $[\text{Os}(\eta^3\text{-CH}_2\text{CMeCH}_2)\text{Cl}(\text{CO})_2(\text{PPh}_3)]$. Interestingly, the iridium complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{Cl}(\text{CO})(\text{PPh}_3)]$ does not react under analogous conditions (40). Scheme 13 summarizes these reactions.

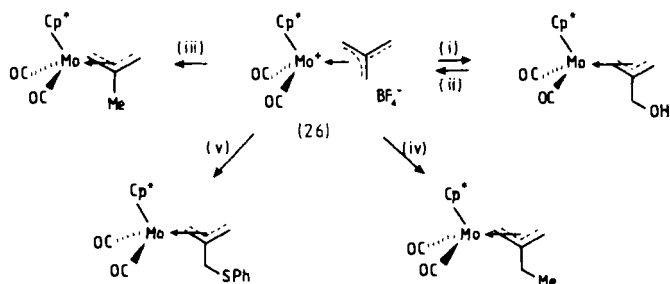


SCHEME 13

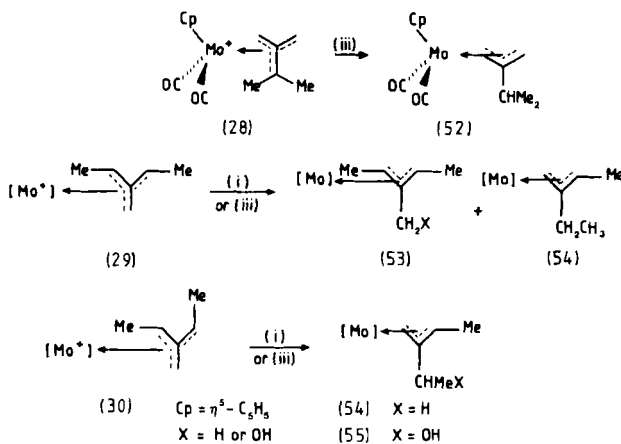
B. With Nucleophiles

The cationic molybdenum trimethylenemethane complex **26** is susceptible to nucleophilic attack at the trimethylenemethane ligand, forming neutral η^3 -allyl complexes (Scheme 14) (25). The methyl-substituted trimethylenemethane cationic complexes also react readily with nucleophiles. Thus complex **28** reacted with sodium borohydride to give the η^3 -allyl complex, **52** where attack of the nucleophile occurred at the methyl-substituted carbon. However, attack of borohydride ion on the complexes **29** and **30** gave the products **53**, ($X = \text{H}$) and **54** due to attack of the nucleophile at both unsubstituted and substituted carbons. Similar results were obtained with hydroxide ion as the nucleophile. Thus the cation **29** reacts regioselectively at the unsubstituted carbon to give the alcohol **53** ($X = \text{OH}$), whereas the reaction of **30** with hydroxide ion gave the product **55** where attack has occurred at a substituted carbon atom.

A combination of steric and electronic effects are thought to control the position of nucleophilic attack on the trimethylenemethane ligand (25). We have found (66) that the cationic iridium complexes are less prone to nucleophilic attack at the trimethylenemethane ligand. The addition of



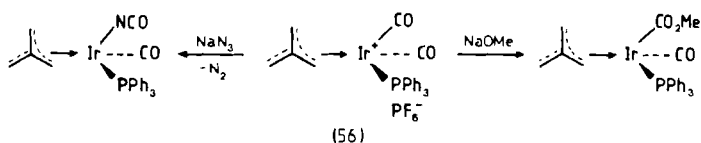
(i) ^-OH ; (ii) HBF_4 , Propionic anhydride; (iii) BF_4^- ; (iv) CuMe_2^- ;
 (v) SPh^- $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$.



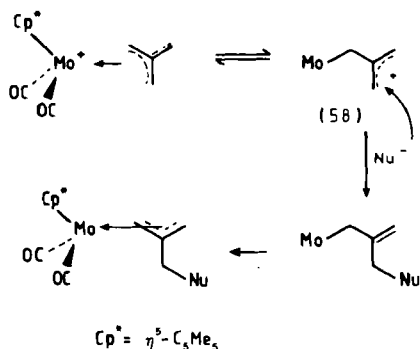
$[\text{Mo}^+] = [\text{Mo}(\text{CO})_2(\eta^5\text{-C}_5\text{Me}_5)]^+$

SCHEME 14

sodium methoxide to a solution of $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_2(\text{PPh}_3)]\text{PF}_6$ (**56**) resulted in nucleophilic attack of the methoxide anion at the carbonyl group, affording the alkoxycarbonyl complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO}_2\text{Me})(\text{CO})(\text{PPh}_3)]$. Similarly, treating **56** with sodium azide gave the isocyanate complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{NCO})(\text{CO})(\text{PPh}_3)]$. Attack by azide ion at the carbonyl ligand followed by loss of nitrogen and a rearrangement accounts for the formation of this product. In contrast to the bis(carbonyl) iridium complex **56** the bis(phosphine) complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PPh}_3)_2]\text{PF}_6$ (**57**) did not react with either sodium methoxide or sodium azide under analogous conditions. A combination of steric and electronic effects resulting from triphenylphosphine ligands in this complex accounts for the lack of reactivity of the carbonyl ligand to nucleophilic attack.



A possible explanation for this differing reactivity of the iridium and molybdenum complexes is that the trimethylenemethane ligand is not firmly coordinated to the molybdenum atom, the protons of the trimethylenemethane fragment being interconverted at room temperature on the NMR time scale. To explain this proton equivalence of the η^4 -trimethylenemethane hydrogens, Green *et al.* (25) proposed that slippage of the η^4 -trimethylenemethane fragment to an η^1 -arrangement (58) occurs. It is possible that the nucleophile is intercepting this intermediate (Scheme 15). In contrast to the molybdenum complexes the trimethylenemethane ligand is firmly coordinated to the iridium atom in these cationic complexes with no sign of rotation on the NMR time scale, implying a stronger metal to ligand interaction.



$\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$
ligands omitted for clarity

SCHEME 15

C. With Tertiary Phosphines

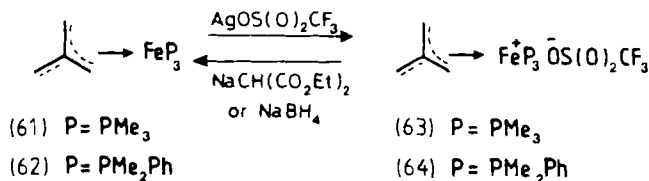
Photolysis of $[\text{Fe}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_3]$ (4) in hexane with trifluorophosphine afforded all three substituted complexes $[\text{Fe}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_{3-x}(\text{PF}_3)_x]$, where x is 1, 2, and 3, which were isolated by GLC (68). The cationic complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PPh}_3)_2]\text{PF}_6$ (57) reacted rapidly at room temperature with various tertiary phosphine ligands (66). Treatment of 57 with 1 mol equivalent of methyldiphenylphosphine afforded a 1:1:1 mixture of the complexes $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PMePh}_2)_2]\text{PF}_6$ (59), $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}$ -

(CO)(PMePh₂)(PPh₃)]PF₆ (**60**), and [Ir{η⁴-C(CH₂)₃}(CO)(PPh₃)₂]}PF₆ (**57**). Addition of 2 mol equivalents of methyldiphenylphosphine to **57** gave the complex **59** in high yield. In a similar manner the complex **57** reacted with 1,2-bis(diphenylphosphino)ethane (dppe) to afford [Ir{η⁴-C(CH₂)₃}(CO)(dppe)]PF₆. These reactions illustrate that the phosphine ligands in these cationic iridium complexes are labile. A carbonyl ligand can be displaced from the complex [Ir{η⁴-C(CH₂)₃}(CO)₂(PPh₃)]PF₆ (**56**) by addition of 1 mol equivalent of methyldiphenylphosphine to afford a 1:1:1 mixture of the complexes **57**, **59**, and **60**.

The ethylene complex [Ir{η⁴-C(CH₂)₃}(η²-C₂H₄)(CO)(PPh₃)]PF₆ also reacted with methyldiphenylphosphine. Initially the complex [Ir{η⁴-C(CH₂)₃}(η¹-C₂H₄PMePh₂)(CO)(PPh₃)]PF₆ was isolated which at 45°C eliminated ethylene to give a 1:1:1 mixture of the three trimethylenemethane complexes **57**, **59**, and **60** (66). Attack by the phosphine at the coordinated ethylene ligand is predicted by the "Rules" laid out for nucleophilic addition to organotransition metal cations containing unsaturated hydrocarbon ligands (75). Although ethylene and trimethylenemethane are *even* polyenes, trimethylenemethane has unpaired electrons in its HOMO, and therefore nucleophilic addition to other even polyenes is preferred.

D. Redox Reactions

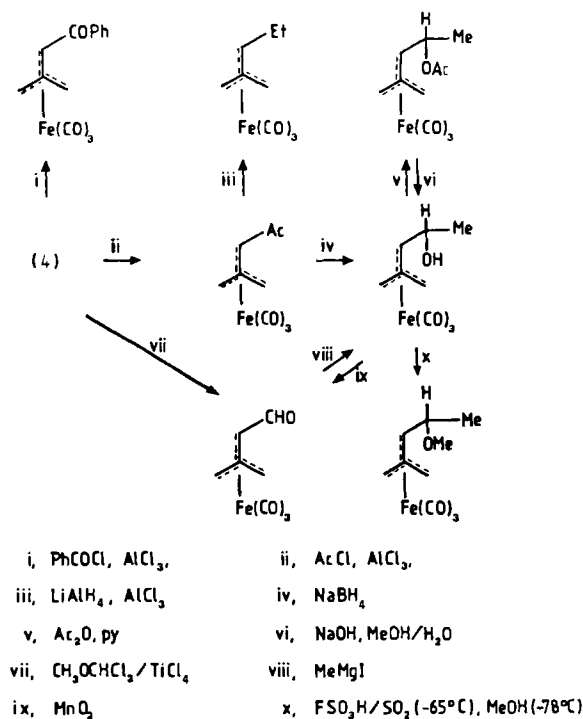
The electron-rich complexes [Fe{η⁴-C(CH₂)₃}(L)₃] (**61**, L = PMe₃; **62**, L = PMe₂Ph) are oxidized with 1 equivalent of silver trifluoromethanesulfonate to afford the cationic 17-electron complexes **63** and **64**, respectively (12). The X-ray structure of **63** has been reported, and the complex adopts the usual staggered conformation as observed for other trimethylenemethane complexes. The green oxidation complexes **63** and **64** react with sodium diethylmalonate or sodium borohydride to reform the original neutral trimethylenemethane complexes **61** and **62** (Scheme 16). The oxidation and reduction processes of these complexes has been investigated by an electrochemical study (12).



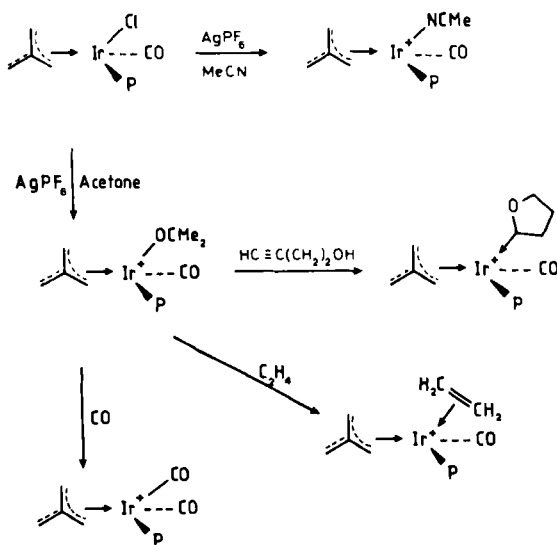
SCHEME 16

E. Modification Reactions

Many new trimethylenemethane complexes are prepared by modifying those that have been synthesized by the methods laid out in Section II. Strictly, these modifications come under the heading of reactivity. Chemical modification of the trimethylenemethane ligand allows a route to a large number of substituted trimethylenemethane complexes of iron, and Scheme 17 summarizes these reactions (9,11,67,73). The iridium complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{Cl}(\text{CO})(\text{PPh}_3)]$ reacts with silver hexafluorophosphate in a donor solvent to give the complexes $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{solvent})(\text{CO})(\text{PPh}_3)]\text{PF}_6$ (solvent = methyl cyanide or acetone) (66). Solutions of these solvate complexes react rapidly with carbon monoxide, ethylene, 3-butyne-1-ol, triphenylphosphine, and triphenylarsine to give a range of cationic complexes in which the η^4 -trimethylenemethane ligand has remained intact and the solvent has been displaced by a neutral two-electron donor ligand (Scheme 18) (66).



SCHEME 17



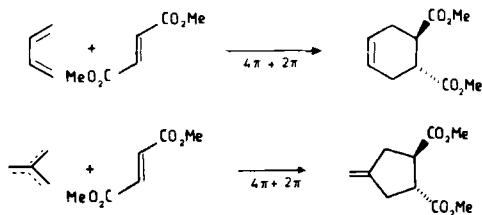
PF_6^- is the counterion. $\text{P}=\text{PPh}_3$

SCHEME 18

V

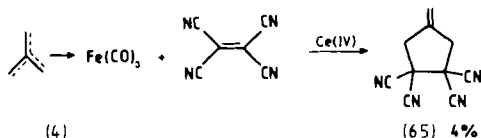
THE ROLE OF TRIMETHYLENEMETHANE IN ORGANIC SYNTHESIS

The cycloaddition of trimethylenemethane to alkenes can be envisaged as the Diels–Alder ($4\pi + 2\pi$) reaction for the synthesis of five-membered rings. This is an attractive ring system to synthesize due to the abundance of five-membered rings found in natural products such as the prostaglandins (76). Cycloaddition reactions also have the advantage of multibond formation occurring almost simultaneously, resulting in structural complexity (77). The strength of the Diels–Alder reaction in cyclohexene chemistry is due to the stereochemical consequences of such a concerted process, and similar stereochemical control may be expected in the related cycloaddition of trimethylenemethane to alkenes (Scheme 19) (78).

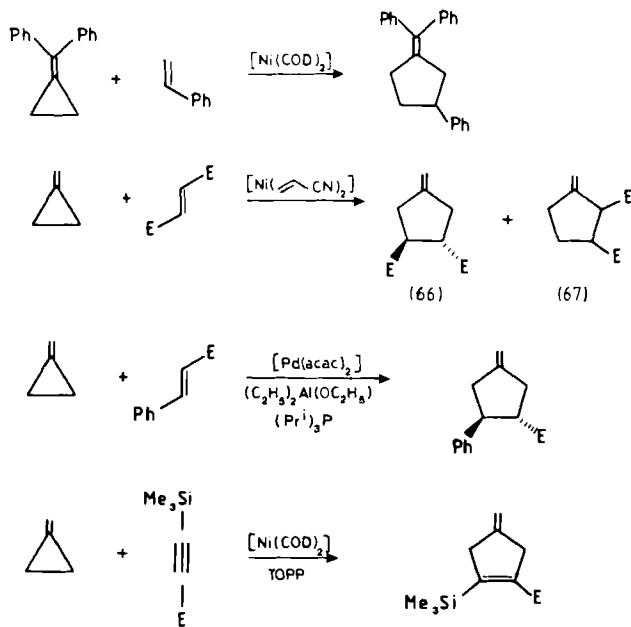


SCHEME 19

A potential source of trimethylenemethane is by the oxidative degradation of a trimethylenemethane metal complex. However this route has met with limited success; the cerium(IV) oxidation of the iron complex **4** in the presence of tetracyanoethylene gave the cycloadduct **65** in very poor yield (*10*). The photolysis of **4** afforded methylenecyclopropane and related products, while in the presence of trapping agents like cyclopentadiene and cyclopentene the expected cycloaddition products were obtained, but in low yields (*79*).



The disrotatory ring opening of substituted methylenecyclopropanes in the presence of $[\text{Fe}_2(\text{CO})_9]$, to give stable η^4 -trimethylenemethane complexes (*18*–*22*) led to the investigation of the transition metal-mediated cycloaddition reactions of methylenecyclopropane. Low-valent nickel and palladium complexes catalyze the codimerization of methylenecyclopropane with both electron-rich and electron-deficient alkenes or alkynes (Scheme 20) (*80*–*90*).



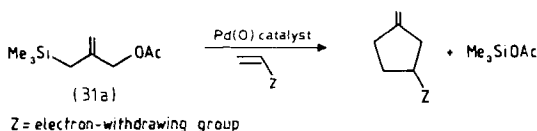
$\text{E} = \text{CO}_2\text{Me}$

TOPP = tris(*o*-biphenyl) phosphite

SCHEME 20

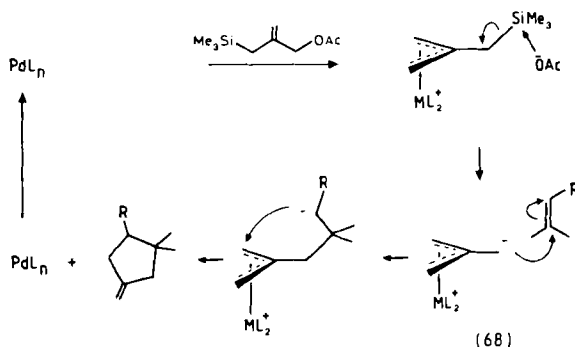
The mechanisms of these codimerization reactions are uncertain. Trimethylenemethane metal complexes have been postulated as intermediates in the palladium-mediated reactions, but in the nickel-catalyzed reactions other intermediates may be involved (81,88). Thus the cycloadduct **66** can be derived from a trimethylenemethane metal complex, but the other product (**67**) cannot. It is presumably formed from an intermediate generated by cleavage of the C-1—C-2 bond of methylenecyclopropane (83).

The ability of palladium(0) catalysis to generate η^3 -allyl complexes by the ionization of allylic acetates (39,91) led Trost and Verhoeven to introduce the functionalized allylic acetate, 3-trimethylsilyl-2-(acetoxymethyl)prop-1-ene (**31a**) as a precursor to a palladium trimethylenemethane complex (6,7). Heating the silyl acetate **31a** in the presence of a catalytic amount of a palladium(0) complex and an electron-deficient alkene results in a cycloaddition of trimethylenemethane to the carbon-carbon double bond (Scheme 21) (6,7).



SCHEME 21

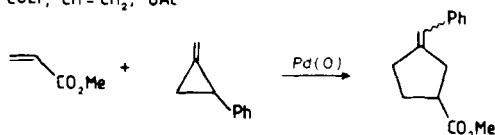
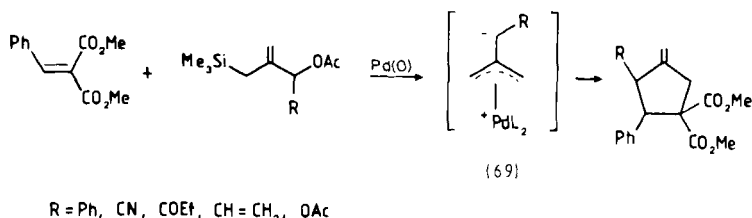
The proposed mechanism for this reaction is thought to proceed via a zwitterionic η^3 -trimethylenemethane intermediate (**68**) (7). Theoretical calculations on $[\text{Pd}(\text{trimethylenemethane})\text{L}_2]$ have demonstrated that the η^3 -trimethylenemethane structure **68** is electronically favored over an η^4 -trimethylenemethane geometry (69,70). Scheme 22 summarizes the presumed mechanism for the formation of this intermediate (**68**). The nucleophilic character of **68** was verified by simple allylic alkylation reactions, and deuterium labeling of the allylic acetate showed that the trimethylenemethane



SCHEME 22

fragment was fluxional and that all three methylene carbons were rapidly interconverting (7).

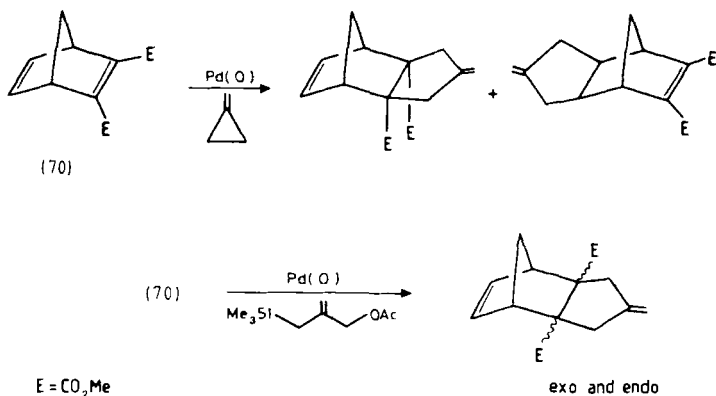
Interestingly, when substituted derivatives of **31a** were used in the cycloaddition reactions, a single regioisomer was isolated, presumably due to preferential reaction via intermediate **69** (71,92–94). This regioselectivity is in contrast to the ring opening reactions of phenyl- and vinyl-substituted methylenecyclopropanes which gave cyclopentane derivatives bearing the substituent almost exclusively on the exocyclic methylene carbon, as shown in Scheme 23 (87,95). The lack of regioselectivity in the catalyzed additions of



SCHEME 23

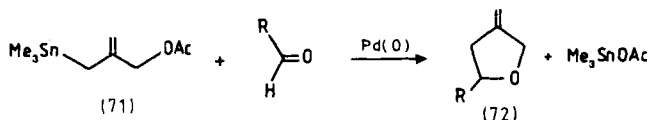
methylenecyclopropane to the norbornadiene **70**, which results in cycloaddition to both double bonds, is in contrast to the reaction of the silyl acetate **31a** with **70** which results in exclusive cycloaddition of trimethylenemethane to the electron-deficient double bond (Scheme 24) (35).

A recent review on the [3 + 2] cycloaddition approaches to five-membered rings via trimethylenemethane presents a possible explanation for the differing

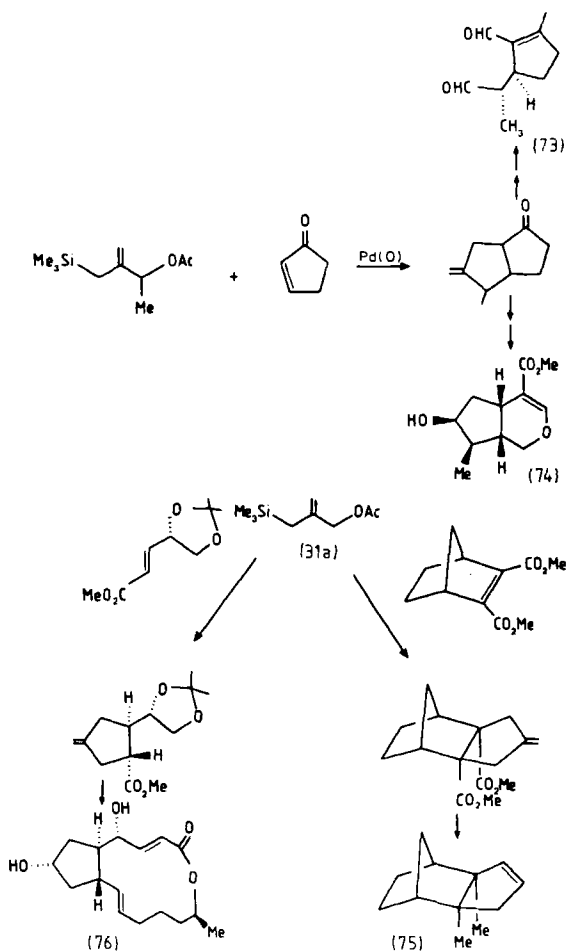


SCHEME 24

reactivity observed in the codimerization reactions of methylenecyclopropanes (35). The trimethyltin acetate **71** also acts as a precursor to trimethylenemethane which undergoes cycloaddition to aldehydes to give substituted methylenetetrahydrofurans **72** (96).



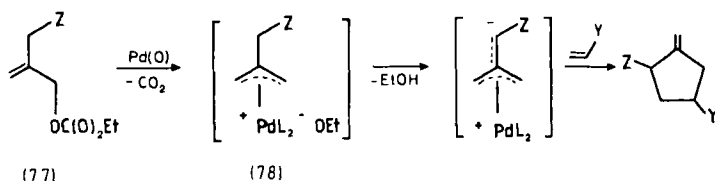
After establishing the general features of the cycloaddition of trimethylenemethane to alkenes, Trost *et al.* explored the implications for retrosyn-



SCHEME 25

thetic analysis of complex molecules. The synthesis of the natural products, chrysmelidial (**73**) (93), loganin aglucone (**74**) (94), albene (**75**) (97), and brefeldin (**76**) (98), use the cycloaddition of trimethylenemethane to alkenes as a means of constructing the five-membered ring. The exocyclic methylene group acts as a versatile functionality for further modifications. Scheme 25 illustrates the principal cycloaddition steps used for the synthesis of these products.

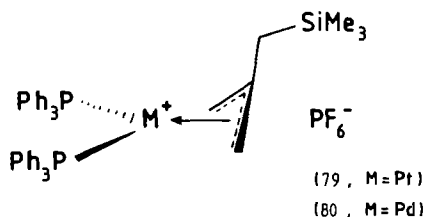
In the special cases of substituents that are good anion-stabilizing groups, the allyl carbonate **77** ($Z = \text{CN}$) serves as a suitable trimethylenemethane precursor. The leaving group generates a sufficiently strong base to effect deprotonation of the η^3 -allyl intermediate **78**, generating a trimethylenemethane complex which reacts with electron-deficient alkenes (Scheme 26) (99).



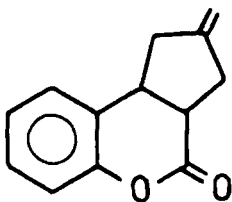
Y, Z = electron-withdrawing groups

SCHEME 26

Evidence for the presence of an intermediate η^3 -trimethylsilylmethylallyl palladium complex (Scheme 22) as a precursor to the catalyst $[\text{Pd}\{\eta^3\text{-C}(\text{CH}_2)_3\}(\text{PPh}_3)_2]$ has been provided by isolation of the complexes **79** and **80** by the reaction of the methanesulfonate **31b** with $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$ and $[\text{Pd}(\text{PPh}_3)_4]$, respectively, in the presence of ammonium hexafluorophosphate (36). Complex **80** is an effective catalyst for the cycloaddition of trimethylenemethane to alkenes. Thus refluxing a toluene solution of **80**, bis(triphenylphosphine) iminium chloride, and triphenylphosphine in the presence of the methanesulfonate **31b** and coumarin afforded the cycloadduct **81** in 23% yield based on **31b** (66).



Attempts to isolate the η^3 -trimethylenemethane complex $[\text{Pt}\{\eta^3\text{-C}(\text{CH}_2)_3\}(\text{PPh}_3)_2]$ by the action of sodium fluoride **79** afforded only the η^3 -2-methylallyl complex $[\text{Pd}\{\eta^3\text{-CH}_2\text{CMeCH}_2\}(\text{PPh}_3)_2]\text{PF}_6$. In contrast, treatment of $[\text{Rh}\{\eta^3\text{-CH}_2\text{C}(\text{CH}_2\text{SiMe}_3)\text{CH}_2\}\text{Cl}(\text{CO})(\text{PMe}_2\text{Ph})_2]\text{BPh}_4$ under

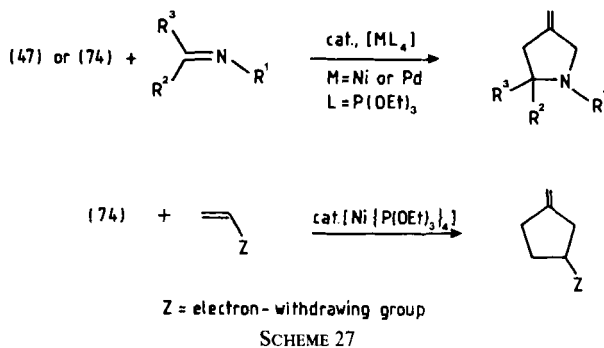


(81)

analogous conditions gave the trimethylenemethane complex $[\text{Rh}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PMe}_2\text{Ph})_2]\text{BPh}_4$ (66).

Trost and Chan have previously reported that the methanesulfonate **31b** serves as a trimethylenemethane equivalent in the palladium-mediated cycloadditions to electron-deficient alkenes although the yield of the cycloadduct was poorer than that obtained using the allylic acetate precursor **31a** (6). In view of the high reactivity of the methanesulfonate **31b** with d^8 and d^{10} metal complexes, the cycloaddition reactions of the trimethylenemethane precursor **31b** have been investigated (100).

Using coumarin as a trap, no cycloadduct can be isolated from the reactions of the methanesulfonate **31b** with the d^8 complexes, *trans*- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$, $[\text{RhH}(\text{PPh}_3)_4]$, $[\text{RhCl}(\text{PPh}_3)_3]$, and $[\text{RuH}_2(\text{PPh}_3)_4]$. However, the methanesulfonate **31b** reacts in the presence of the d^{10} complex $[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$ to afford a catalyzed cycloaddition of trimethylenemethane to imines and electron-deficient alkenes in high yield (100). The cycloaddition of trimethylenemethane to imines is also catalyzed by a palladium(0)/triethylphosphite complex, although the platinum system $[\text{Pt}\{\text{P}(\text{OEt})_3\}_n]$ is not an effective catalyst for these reactions. The general reaction is shown in Scheme 27.



Interestingly $[\text{Pd}(\text{PPh}_3)_4]$, which was so effective in catalyzing the cycloaddition of trimethylenemethane to alkenes, was a poor catalyst for the cycloaddi-

tion of trimethylenemethane to imines. This shows that the choice of ligand is an important factor in these cycloaddition reactions. Trost *et al.* has previously noted that the yields of the cycloadducts of substituted trimethylenemethane with alkenes were improved if the catalyst was switched from $[\text{Pd}(\text{PPh}_3)_4]$ to $[\text{Pd}\{\text{P}(\text{OPr}^i)_n\}]$ (92). The allylic acetate **31a** also serves as a trimethylenemethane equivalent for the cycloaddition to imines in the presence of nickel or palladium phosphite catalysts.

The inability of d^8 metal complexes to catalyze the addition of trimethylenemethane to alkenes or imines is presumably due to the formation of a stable $[\text{M}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{L}_3]$ complex in which all three methylene carbons are strongly coordinated to the metal center. This is not the situation on coordination of trimethylenemethane to a $d^{10}\text{ML}_2$ fragment ($\text{M} = \text{Ni}, \text{Pd},$ or Pt), since an η^3 -trimethylenemethane complex is favored (see Section III).

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Organometallic Chemistry of Molybdenum and Tungsten Supported by Alkoxide Ligands

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I

INTRODUCTION

Organotransition metal chemistry has largely developed with the support of soft, π acceptor ligands such as carbon monoxide, tertiary phosphines, and cyclopentadienyls. Alkoxide ligands, RO^- , share some common features with the above. Like CO, RO^- ligands may occupy either terminal or bridging positions, and relatively facile bridge opening and closing produces fluxional behavior in polynuclear compounds. Bulky alkoxide ligands can be selected to favor specific coordination numbers and geometries in much the same way that bulky phosphines or $\eta^5\text{-C}_5\text{Me}_5$ are used. The proper choice of steric bulk allows coordinative unsaturation to be introduced into ground states or into thermally accessible intermediates by alkoxide-bridge opening.

Alkoxide ligands are in many ways complementary to traditional, soft, π -acceptor ligands. As a result of their uninegative charge and π -donating properties, π^x where $0 < x < 4$, alkoxide ligands stabilize early transition metals in their mid-to-high oxidation states. Unlike the case with CO or PR_3 , alkoxide-ligand dissociation is not typically observed (in nonpolar solvents); thus, steric effects are more easily designed and maintained.

Alkoxide ligands are electronically flexible. The degree of π donation can respond to the needs of a metal atom, which may change with substrate uptake or release. The equilibrium of Eq. (1) is illustrative. The position of equilibrium in Eq. (1) is determined by the metal, Mo versus W, the bulkiness of R and L,



M = Mo or W, L = pyridine, PR_3 , etc.

the nature of L, and the temperature (*T*). The formal electron count at each metal does not change with Lewis base association or dissociation. In forming one metal-ligand σ bond, $\text{M}-\text{L}$, one $\text{M}-\text{OR}$ π bond is sacrificed;

on breaking the M—L σ bond, one M—OR π bond is formed. In general, M—OR π bonding is delocalized over all M—OR bonds, although symmetry considerations, trans influences, and neighboring ligands may oppose this and cause M—OR π bonds to be localized. The degree of π donation of an alkoxide increases with the M—O—C angle. Since the M—O—C angle is sensitive to steric factors and internal steric pressure, the electron-releasing strength of alkoxide ligands, both σ and π , follows the order $t\text{-BuO} > i\text{-PrO} > t\text{-BuCH}_2\text{O} > \text{EtO}$.

Alkoxide π donation has pronounced effects on physicochemical properties of alkoxide complexes and the reactivities of ancillary ligands. The Lewis acidity of vacant coordination sites at a metal is buffered. Agostic M---H—C interactions (2) are muted. RO-to-M π donation raises the energy of filled metal d_π orbitals, which in turn enhances metal d_π -to-ligand π^* backbonding to ancillary ligands with π^* -acceptor orbitals.

Finally, we note that a number of isolobal relationships may be found (3). The d^2 M(OR)₄ unit is isolobal with 16-electron organometallic fragments, e.g., Fe(CO)₄, and the d^3 M(OR)₃ unit is isolobal with 15-electron fragments such as Co(CO)₃ and CpM(CO)₂, where M = Mo and W. Thus for molybdenum and tungsten, alkoxide ligands are well-suited to the development of mononuclear and cluster organometallic chemistry.

This article classifies the organometallic chemistry of molybdenum and tungsten alkoxides, which is becoming a mature research field, according to ligand type. We have attempted to give a comprehensive description of areas that have not been reviewed previously and to give an overview and recent advances in areas that are covered in existing reviews.

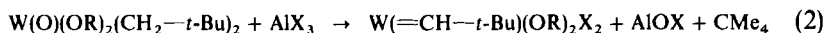
II

MONONUCLEAR ALKYLIDENE COMPLEXES

A. Synthesis and Properties

1. Preparation by Alkane Elimination

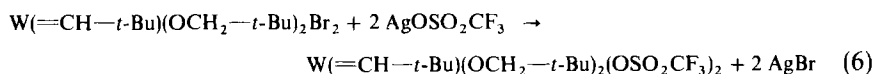
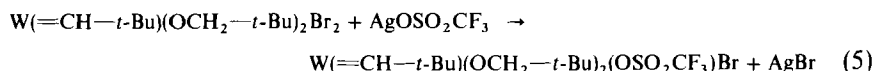
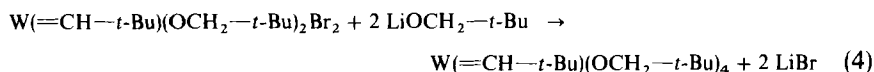
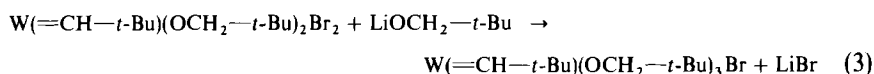
Osborn found that tungsten alkyls react with aluminum halides according to Eq. (2) (4). Although not completely general, the method succeeds for R = CH₂—*t*-Bu, X = Cl, Br, or I, and R = *i*-Pr, X = Cl or Br (5). The pentacoordinate alkylidene complexes were assigned trigonal bipyramidal



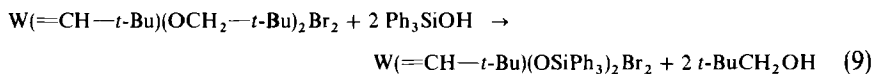
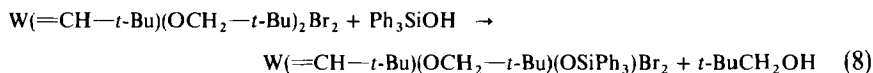
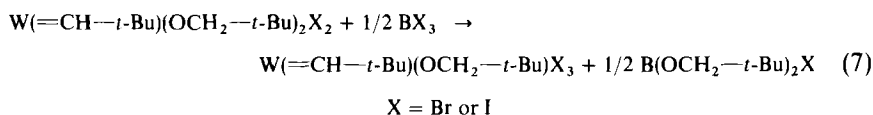
geometries with axial halide, and equatorial alkoxide and $\text{CH}-t\text{-Bu}$ ligands on the basis of spectroscopic data.

2. Preparation by Substitution Reactions of $\text{W}(=\text{CH}-t\text{-Bu})(\text{OR})_2\text{X}_2$

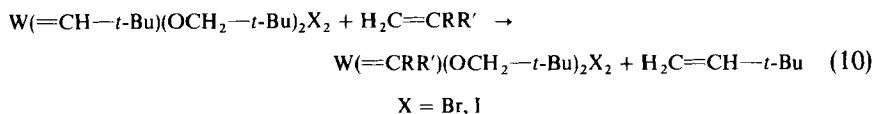
The axial halide ligands of $\text{W}(=\text{CH}-t\text{-Bu})(\text{OR})_2\text{X}_2$ can be replaced as shown in Eqs. (3)–(6) (5). The trifluoromethanesulfonate ligands



in $\text{W}(=\text{CH}-t\text{-Bu})(\text{OCH}_2-t\text{-Bu})_2(\text{OSO}_2\text{CF}_3)\text{Br}$ and $\text{W}(=\text{CH}-t\text{-Bu})(\text{OCH}_2-t\text{-Bu})_2(\text{OSO}_2\text{CF}_3)_2$ remain strongly coordinated in bromobenzene solution. The alkoxide ligands of $\text{W}(=\text{CH}-t\text{-Bu})(\text{OCH}_2-t\text{-Bu})_2\text{X}_2$ are substituted by the reactions in Eqs. (7)–(9).



Finally, the neopentylidene ligand can be exchanged by stoichiometric alkene metathesis, Eq. (10). The reaction appears to be quite general (5), providing new complexes with benzyldiene, *n*-butylidene, and cyclopentylidene



ligands, as examples. The *catalytic* metathesis activity of $W(=CRR')-(OCH_2-t-Bu)_2X_2$ and related complexes will be discussed in Section II,B,1.

3. Trends in Spectroscopic Data

Equations (2)–(4) provide the homologous series $W(=CH-t-Bu)-(OCH_2-t-Bu)_nBr_{4-n}$ for $n = 1-3$. The NMR data for this series reveal the effects of the powerful π -donor alkoxide ligands and are recorded in Table I (6) along with the data for a related compound, $W(=CH-t-Bu)-(OCH_2-t-Bu)I_3$ (5). The successive replacement of alkoxide ligands by the poor π -donor halide ligands results in a progressive and substantial downfield shift in the resonance for the alkylidene C_α (Table I), reflecting an increasing electron deficiency at this site. At the same time, the $^{183}W-^{13}C$ coupling constant, a qualitative measure of the strength of the $W=C$ bond, is progressively decreased. This is likely due to the lessened ability of tungsten to backbond with the alkylidene acceptor orbital.

All Table I compounds are *formally* unsaturated, 12-electron complexes. Unsaturated alkylidene complexes frequently exhibit agostic (2) $M---H-C$ interactions with the alkylidene H_α , which can be identified by atypically low values for the $^{13}C_\alpha-^1H_\alpha$ coupling constant (7). Only the last two entries in Table I, in which *three* alkoxide ligands are replaced by halides, show $^1J_{C-H}$ values small enough to suggest perhaps a weak $W---H_\alpha-C_\alpha$ agostic interaction (7). Thus, electronic unsaturation in such alkoxide complexes is relieved by the strong π -donor character of the alkoxides; the desire of the metal to seek electron density from adjacent $C-H$ bonds is removed. The $^1H_\alpha$ chemical shifts do not follow a clear trend (Table I), but the data indicate that resonances may appear in a fairly wide range.

TABLE I
SELECTED NMR DATA FOR $W(=CH-t-Bu)(OCH_2-t-Bu)_nX_{4-n}$ ^a

Complex	$\delta_{^{13}C_\alpha}$ (ppm)	$^1J_{WC_\alpha}$ (Hz)	$^1J_{C_\alpha H_\alpha}$ (Hz)	$\delta_{^1H_\alpha}$ (ppm)
$W(=CH-t-Bu)(OCH_2-t-Bu)_4$	252.6	192	137	7.90
$W(=CH-t-Bu)(OCH_2-t-Bu)_3Br$	273.7	182	135	9.76
$W(=CH-t-Bu)(OCH_2-t-Bu)_2Br_2$	297.2	159	135	11.12
$W(=CH-t-Bu)(OCH_2-t-Bu)Br_3$	308.2	146	127	8.54
$W(=CH-t-Bu)(OCH_2-t-Bu)I_3$	321.5	—	114	6.66

^a Adapted with permission from Ref. 6, J. Kress, A. Aguero, and J. A. Osborn, *J. Mol. Cat.* **36**, 1 (1986). Copyright 1986 Elsevier Sequoia S.A.

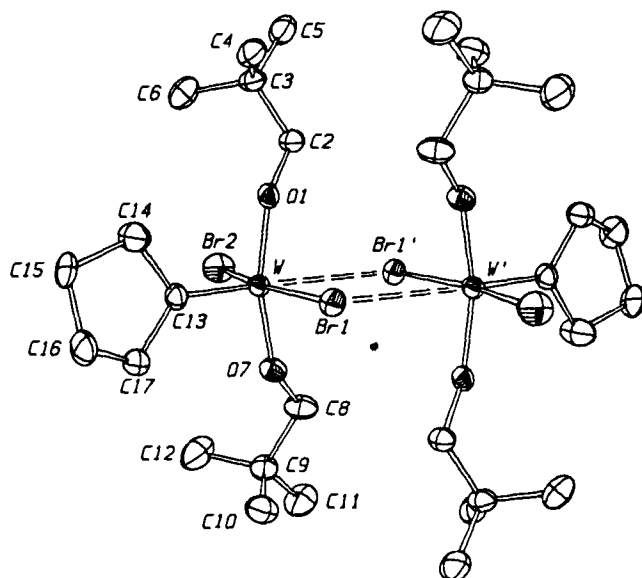
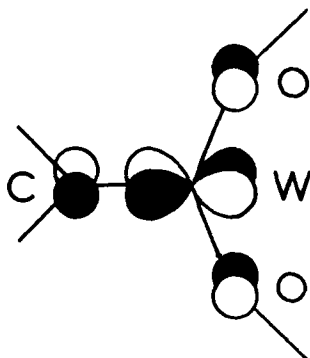


FIG. 1. ORTEP view of $W[=C(CH_2)_3CH_2](OCH_2-t-Bu)_2Br_2$. Important bond distances are listed in the text. Used with the permission of J. A. Osborn, who retains all rights (8).

4. Structure

The molecular structure of $W[=C(CH_2)_3CH_2](OCH_2-t-Bu)_2Br_2$ has been determined by X-ray crystallography (8), and an ORTEP view is shown in Fig. 1. The compound exists as a weakly associated dimer in the solid state that is held together by asymmetric Br bridges. There is no metal-metal bond [$W-W' = 4.3414(4) \text{ \AA}$]. Spectroscopic data indicate that dissociation into monomers occurs in solution. Several structural features characterize the influence of the alkoxide ligands. The $W-O$ distances are unusually short [$1.816(4)$ and $1.828(4) \text{ \AA}$], and the $W-O-C$ angles are large [$145.4(4)$ and $145.6(4)^\circ$], evidencing strong $O \rightarrow W$ π overlap. The alkylidene $W-C-13$ distance is also short [$1.889(5) \text{ \AA}$], consistent with a double bond.

The most revealing aspect is the coplanarity of C-14, C-13, C-17, W, O-1, and O-7. The alkylidene ligand can be considered as a neutral, singlet, two-electron donor fragment with a low-lying empty p orbital. A qualitative molecular orbital scheme for an analogous alkylidene complex has been reported (9). It is clear from Fig. 1 that the alkoxide and alkylidene ligands are π bonding to the *same* $W d$ orbital as shown by **1**, with the alkoxide ligands functioning as donors and the alkylidene ligand as an acceptor. Thus



1

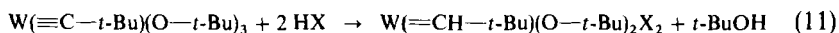
tungsten is the conduit that funnels electron density from the electron-rich alkoxides to the electron-deficient alkylidene. In molecular-orbital terms, an occupied oxygen p orbital combination and an occupied tungsten d orbital undergo a two-orbital, four-electron destabilizing interaction that lowers the energy of the oxygen-centered orbital and raises the energy of the tungsten-centered orbital. In turn, the tungsten-centered orbital and the empty alkylidene p orbital undergo a two-orbital, two-electron stabilizing interaction (9) that pushes the tungsten-centered orbital back down and raises the carbon-centered orbital. The net effect is the stabilization of occupied oxygen-centered orbitals and the destabilization of the empty carbon-centered orbital.

If the alkylidene fragment were rotated 90° into coplanarity with Br-2, W, and Br-1, π bonding would be substantially disrupted. Bromide lone pair orbitals are diffuse, W—Br bond distances are long; consequently, bromide is a less effective π donor. At the same time, alkoxide lone pair electrons would lose a mechanism for stabilization, making the total energy of the second conformation higher. On the basis of this argument, the barrier to alkylidene rotation should be high, and is estimated to be > 22 kcal/mol (6). However, replacement of a Br with an OR ligand should lower the barrier, because better net π bonding would result at the latter conformation. In fact, the barriers to alkylidene rotation in $W(=CHR)(OCH_2-t-Bu)_3X$ compounds are 12–16 kcal/mol (6).

5. Other Preparations

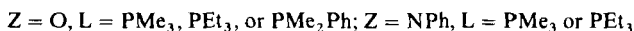
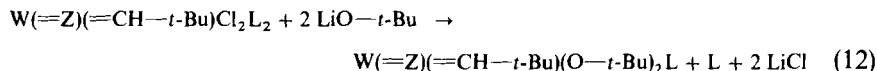
Schrock and Freudenberger have prepared alkylidene complexes, analogous to the Osborn compounds above, by the protonation of alkylidyne

complexes [Eq. (11)] (10). Alkylidyne complexes will be covered in Section III. Similar reactions fail for $X = \text{Br}$ or Cl when the alkylidyne ligand has



β -hydrogens, unless pyridine (py) is also present. Then compounds of type $\text{W}(\equiv\text{CHCH}_2\text{R})(\text{O}-t\text{-Bu})_2\text{X}_2(\text{py})$ are isolated, with pyridine coordinated trans to the alkylidene ligand. Unstable alkylidene complexes are obtained from reactions of β -hydrogen-containing alkylidyne complexes and carboxylic acids, which will be discussed in Section II,B,4.

Schrock and Pedersen have also reported the synthesis of oxo (11) and imido alkylidene complexes (12) according to Eq. (12). The oxo complexes are thermally unstable, decomposing within a few minutes at room temperature.



The imido complexes are considerably more stable. The *four*-coordinate imido complex $\text{W}(\equiv\text{CH}-t\text{-Bu})[\equiv\text{N}-2,6\text{-C}_6\text{H}_3(i\text{-Pr})_2][\text{OCMe}(\text{CF}_3)_2]_2$ is prepared from $\text{W}(\equiv\text{CH}-t\text{-Bu})[\equiv\text{N}-2,6\text{-C}_6\text{H}_3(i\text{-Pr})_2]\text{Cl}_2(\text{dme})$ (13). Schrock's use of fluoroalkoxide ligands has produced a number of interesting results (see Sections II,B,1, III, and IV).

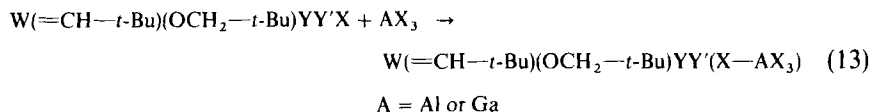
B. Reactivity

1. Alkene Metathesis

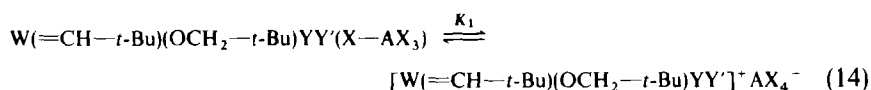
The most important aspect of the reactivity of alkylidene alkoxide complexes is their ability to catalyze alkene metathesis. This behavior was suggested for $\text{W}(\equiv\text{CH}-t\text{-Bu})(\text{OCH}_2-t\text{-Bu})_2\text{X}_2$ by the stoichiometric olefin metathesis reaction of Eq. (10). Indeed, the complexes $\text{W}(\equiv\text{CH}-t\text{-Bu})(\text{OCH}_2-t\text{-Bu})\text{YY}'\text{X}$ ($\text{Y} = \text{halide or } \text{OCH}_2-t\text{-Bu}$, $\text{X} = \text{halide}$) are capable of metathesizing 2-pentene, terminal alkenes, and even functionalized alkenes such as olefinic esters (5,6). Except for $\text{W}(\equiv\text{CH}-t\text{-Bu})(\text{OCH}_2-t\text{-Bu})\text{Br}_3$, however, the rate of metathesis is fairly slow. The progressive replacement of halides by alkoxides *decreases* the activity of these five-coordinate, neutral compounds.

Highly active catalysts are generated by adding Lewis acids to $\text{W}(\equiv\text{CH}-t\text{-Bu})(\text{OCH}_2-t\text{-Bu})\text{YY}'\text{X}$. The addition of 0 to 1 equiv of Lewis acid results in linear displacements of NMR resonances pertaining to the alkylidene complex and a concurrent linear increase in the rate of alkene

metathesis (14). The conductivity of solutions on addition of 1 equiv of Lewis acid remains low. These data (14) are consistent with 1:1 adduct formation as shown in Eq. (13). However, the conductivity of such solutions is not zero,

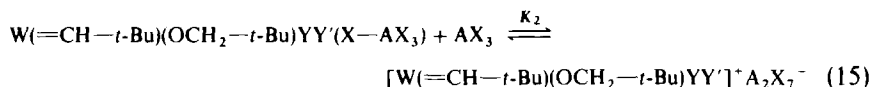


suggesting the equilibrium of Eq. (14), which may lie as far as 15% toward the four-coordinate cation. It thus appears likely that the true metathesis catalyst



in the presence of Lewis acids is the cationic species [Eq. (14)] and that K_1 is small.

Support for this proposal is gained by adding greater than 1 equiv of AX_3 to solutions of $\text{W(=CH-}t\text{-Bu)(OCH}_2\text{-}t\text{-Bu)YY'X}$ (14). Displacement of NMR resonances continues, but in a nonlinear fashion, and plots of such displacements versus the amount of added Lewis acid (0 to 6 equiv) clearly show discontinuities at 1 equiv, indicating the emergence of a second species. After 1 equiv of added Lewis acid, metathesis rates increase dramatically and nonlinearly, and the conductivities asymptotically approach (with 6 equiv AX_3) the expected values for a 1:1 electrolyte. These data suggest the equilibrium of Eq. (15), where K_2 is small.



In contrast to the neutral, five-coordinate $\text{W(=CH-}t\text{-Bu)(OCH}_2\text{-}t\text{-Bu)YY'X}$, the catalytic activity for $[\text{W(=CH-}t\text{-Bu)(OCH}_2\text{-}t\text{-Bu)YY'}]^+$ increases by replacing halides with alkoxides (Y and Y'). The latter observation is related to the generally low values of the equilibrium constants K_1 and K_2 [Eqs. (14) and (15)]. The π donation from alkoxide ligands stabilizes the four-coordinate cations, thereby increasing the values of K_1 and K_2 (6). Higher concentrations of the catalytically active cations result. The opposite trend observed for the neutral catalysts (i.e., without Lewis acid) is probably due to decreasing electrophilicity on substitution of halides with alkoxides (6).

The neutral and cationic catalyst systems have certain similarities. In both cases *Z:E* selectivity in the alkene products is low, although somewhat higher for the neutral catalysts (maximum value around 3.1) (6). In neither case can

intermediate alkene alkylidene or metallacyclobutane complexes be observed, but the propagating alkylidene complexes are easily detected (4,6). Both systems will polymerize norbornene; in the cationic system a "living" polymer was prepared (15).

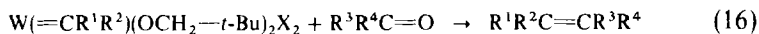
As expected from the results of Osborn described above, the complexes $W(=CH-t-Bu)(O-t-Bu)_2X_2$ ($X = \text{halide}$) reported by Schrock are not active alkene metathesis catalysts in the absence of Lewis acids (16). However, the *four*-coordinate, *neutral* complex $W(=CH-t-Bu)[=N-2,6-C_6H_3-(i-Pr)_2][OCMe(CF_3)_2]_2$ reacts stoichiometrically with alkenes to give new alkylidene or metallacyclobutane complexes and rapidly catalyzes the metathesis of *cis*-2-pentene without added Lewis acid (13).

2. Coordination of Lewis Bases

The solid-state structure of $W[=C(CH_2)_3CH_2](OCH_2-t-Bu)_2Br_2$ (Fig. 1) implies the availability of a coordination site *trans* to the alkylidene ligand (8). Thus pyridine and $W[=C(CH_2)_3CH_2](OCH_2-t-Bu)_2Br_2$ react to give the expected *trans* product $W[=C(CH_2)_3CH_2](OCH_2-t-Bu)_2Br_2(py)$, which slowly rearranges to place the alkylidene and pyridine in *cis* positions (8). The complexes $W(=CRR')(OCH_2-t-Bu)_2X_2$ form 1:1 adducts with a variety of Lewis bases including alkenes, but the isolation of such adducts requires fairly good donors, like pyridine (6) (see also Section II,A,5). These observations help to rationalize the low alkene metathesis activity of $W(=CH-t-Bu)(OCH_2-t-Bu)YY'X$. The initial complexation of alkene gives an octahedral complex with *trans* alkene and alkylidene ligands, from which metallacyclobutane formation and subsequent metathesis cannot proceed directly. In contrast, the four-coordinate $[W(=CH-t-Bu)(OCH_2-t-Bu)YY']^+$ has *two* available coordination sites for incoming alkene, and a resulting five-coordinate alkene alkylidene complex is likely to be much more configurationally mobile. Of course, the greater overall electrophilicity of the cation probably contributes to its greater activity.

3. Wittig Chemistry

The alkylidene complexes $W(=CR^1R^2)(OCH_2-t-Bu)_2X_2$ react with aldehydes and ketones to give alkene products in a Wittig-type synthesis [Eq. (16)] (17). By comparison, $W(=CR^1R^2)(OCH_2-t-Bu)_4$ is a much more



powerful reagent that reacts with esters or lactones at room temperature and with amides at 50°C (17). Thus, replacement of halides by the π -donor

alkoxide ligands significantly increases the nucleophilicity of the alkylidene C_α . Interestingly, a Wittig-type reaction does not interfere with the metathesis of $CH_2=CH(CH_2)_2CO_2Me$ by $W(=CH-t-Bu)(OCH_2-t-Bu)_2I_2$ (5), but may represent a mechanism for eventual catalyst deactivation (6).

4. Rearrangement Chemistry

The several examples of alkylidene complexes with β -hydrogens prepared by Osborn's group are unprecedented for unsaturated complexes (8). In fact, there is ample literature precedent for the rearrangement of β -hydrogen-containing alkylidene ligands to alkene ligands, by 1,2-H migration (18). The thermolysis of $W[=\overline{C(CH_2)_3CH_2}](OCH_2-t-Bu)_2Br_2$ does give cyclopentene by a unimolecular process, but the tungsten product(s) is not identified (8). Schrock and Freudenberger have reported the preparation of $W(=CHCH_2R)(O-t-Bu)_2(OCOPh)_2$ by reactions analogous to Eq. (11) (see Section II,A,5, $R = H$ or Me) (10). These complexes are unstable, rearranging by what appear to be second-order kinetics to the alkene complexes $W(CH_2=CHR)(O-t-Bu)_2(OCOPh)_2$. The rearrangement can be catalyzed by added benzoic acid. The products are unusual examples of tungsten(IV) alkene complexes, and the alkene ligands are readily displaced by other alkenes or PMe_3 .

III

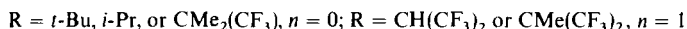
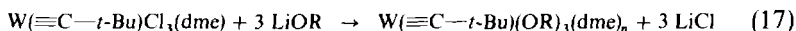
MONONUCLEAR ALKYLIDYNE COMPLEXES

A. Synthesis and Properties

1. Preparation from Halide Complexes

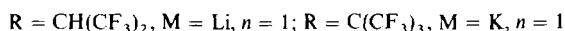
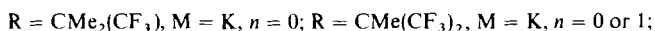
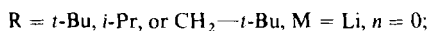
Schrock *et al.* originally prepared $W(\equiv C-t-Bu)(O-t-Bu)_3$ by the substitution reaction of $LiO-t-Bu$ with $[NEt_4]^+[W(\equiv C-t-Bu)Cl_4]^-$ (19,20). The stable, sublimable, pale-yellow $W(\equiv C-t-Bu)(O-t-Bu)_3$ was the first alkylidyne alkoxide complex, and it was assigned a tetrahedral geometry (21). The best spectroscopic evidence for alkylidyne ligands is found by ^{13}C NMR. In this case the chemical shift of the alkylidyne C_α is 271 ppm, within the range characteristic of the $W\equiv CR$ unit (20,22).

Subsequently, the general procedure of Eq. (17) was reported, which provides several examples of neopentylidyne complexes supported by various alkoxide ligands (22–24). In two cases with fluoroalkoxide ligands, sublimable



η^2 -dme adducts are obtained; the less electron-releasing alkoxides increase the electrophilicity of tungsten, and thus its affinity for Lewis bases. The adducts were assigned mer octahedral geometries on the basis of spectroscopic properties.

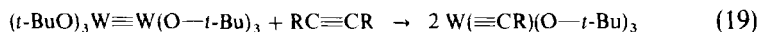
Isostructural molybdenum-neopentylidyne complexes are prepared similarly, as shown by Eq. (18) (25,26). Syntheses using fluoroalkoxide reagents (MOR_F) are sensitive to conditions; in several cases, a change of



solvent or alkali metal results in the isolation of partially substituted products $\text{Mo}(\equiv\text{C}-t\text{-Bu})(\text{OR}_F)_2\text{Cl}(\text{dme})$ (26).

2. Alkyne-Cleavage Reactions

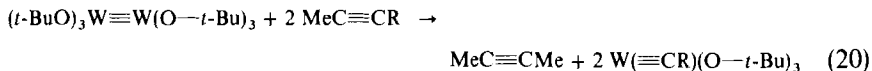
A complementary procedure was discovered by Schrock that provides a variety of alkylidyne ligands, as shown by Eq. (19) (22,27). The symmetrical cleavage reaction of Eq. (19) proceeds readily when R is a simple alkyl group



and is also successful for several functionalized alkynes, such as $\text{R} = \text{CH}_2\text{NMe}_2$, CH_2OMe , and NEt_2 . The latter are more difficult to cleave, and rates and product yields are generally increased by the presence of nitrogen donor ligands like pyridine (py) or quinuclidine (quin). In these cases, the adducts $\text{W}(\equiv\text{CR})(\text{O}-t\text{-Bu})_3(\text{py})$ or $\text{W}(\equiv\text{CR})(\text{O}-t\text{-Bu})_3(\text{quin})$ are obtained (see Section III,B,2).

The cleavage of alkynes is not limited to $\text{W}_2(\text{O}-t\text{-Bu})_6$. Complexes $\text{W}_2(\text{O}-i\text{-Pr})_6(\text{HNMe}_2)_2$ and $\text{W}_2[\text{OCMe}_2(\text{CF}_3)]_6$ will cleave 3-hexyne and 2-butyne, respectively, to give $\text{W}(\equiv\text{CEt})(\text{O}-i\text{-Pr})_3(\text{HNMe}_2)$ (24,28a) and $\text{W}(\equiv\text{CMe})[\text{OCMe}_2(\text{CF}_3)]_3$ (24) (see also Section VI,B,1). However, several d^3-d^3 triply bonded dimers do not cleave internal alkynes: $\text{W}_2(\text{NMe}_2)_6$, $\text{W}_2(\text{CH}_2\text{SiMe}_3)_6$, $\text{W}_2\text{Cl}_6(\text{thf})_4$, 1,2- $\text{W}_2\text{Cl}_2(\text{NMe}_2)_4$, and $\text{Mo}_2(\text{O}-t\text{-Bu})_6$ (27). To date, cleavage of internal alkynes is found only with dinuclear tungsten alkoxides [and aryloxides (28b)].

Equation (19) fails for bulky R groups such as CMe_3 , SiMe_3 , and SnMe_3 , but alkylidyne complexes bearing large groups can be prepared by the cleavage of unsymmetric alkynes (22). For example, reaction of $\text{W}_2(\text{O}-t\text{-Bu})_6$ and $\text{MeC}\equiv\text{CCMe}_3$ produces the expected 1:1 ratio of $\text{W}\equiv\text{CMe}$ and $\text{W}\equiv\text{CCMe}_3$ compounds. Unsymmetric alkyne cleavage is synthetically useful when at least 2 equiv alkyne are employed and the low-boiling alkyne product is removed *in vacuo*, as shown in Eq. (20). Clearly, Eq. (20) chemistry is more

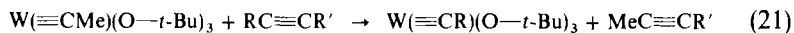


complicated than simple alkyne cleavage, requiring an alkyne metathesis step as well. Alkyne metathesis is the subject of Sections III,A,3 and III,B,1. Several functionalized alkylidyne ligands are prepared from unsymmetric alkynes, and these reactions are frequently best done in the presence of pyridine or quinuclidine (22).

Reactions of terminal alkynes, $\text{RC}\equiv\text{CH}$, and $\text{W}_2(\text{O}-t\text{-Bu})_6$ afford $\text{W}(\equiv\text{CR})(\text{O}-t\text{-Bu})_3$ as the only isolable product unless quinuclidine is present (22). Then the 1:1 mixture of $\text{W}(\equiv\text{CR})(\text{O}-t\text{-Bu})_3(\text{quin})$ and $\text{W}(\equiv\text{CH})(\text{O}-t\text{-Bu})_3(\text{quin})$ is obtained. Base-free $\text{W}(\equiv\text{CH})(\text{O}-t\text{-Bu})_3$ is highly unstable, as is its pyridine adduct (see Section V,B,2). Complex $\text{W}(\equiv\text{CH})(\text{O}-t\text{-Bu})_3(\text{quin})$ can be isolated from the reaction of $\text{W}_2(\text{O}-t\text{-Bu})_6$, $\text{HC}\equiv\text{CH}$, and quinuclidine. Similar results are obtained from $\text{Mo}_2(\text{O}-t\text{-Bu})_6$ and *terminal* alkynes, giving $\text{Mo}(\equiv\text{CR})(\text{O}-t\text{-Bu})_3$ or the 1:1 mixture of adducts with quinuclidine (29). As stated above, $\text{Mo}_2(\text{O}-t\text{-Bu})_6$ will not cleave internal alkynes, nor will it cleave $\text{HC}\equiv\text{CH}$ in the presence or absence of quinuclidine.

3. Stoichiometric Alkyne Metathesis

Equation (20) involves, as one fundamental step, a stoichiometric alkyne metathesis reaction conforming to Eq. (21). Indeed, $\text{W}(\equiv\text{CMe})(\text{O}-t\text{-Bu})_3$ is a synthetically useful precursor to alkylidyne complexes, reacting with



$\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$, for example, to give $\text{W}(\equiv\text{CSiMe}_3)(\text{O}-t\text{-Bu})_3$ according to Eq. (21) (22). Similar reactions occur between $\text{Mo}(\equiv\text{C}-t\text{-Bu})(\text{O}-t\text{-Bu})_3$ and *terminal* alkynes, $\text{RC}\equiv\text{CH}$, providing the complexes $\text{Mo}(\equiv\text{CR})(\text{O}-t\text{-Bu})_3$ where $\text{R} = i\text{-Pr}$, $n\text{-Pr}$, and Ph (26). Unlike $\text{Mo}(\equiv\text{CR})(\text{O}-t\text{-Bu})_3$, the fluoroalkoxide complexes $\text{Mo}(\equiv\text{C}-t\text{-Bu})(\text{OR}_F)_3(\text{dme})_n$ will undergo stoichiometric alkyne metathesis with *internal* alkynes to give alkylidyne complexes $\text{Mo}(\equiv\text{CR})(\text{OR}_F)_3(\text{dme})_n$, where $\text{R} = \text{Me}$, Et , $n\text{-Pr}$, and

Ph (25,26). Reactions of $W(\equiv CR)(OR_F)_3(dme)_n$ and $Mo(\equiv CR)(OR_F)_3(dme)_n$ with internal and terminal alkynes, respectively, give alkylidyne complexes only in certain cases, which limits their synthetic utility (23,26). However, other interesting products, discussed in Sections IV,A,2,a and IV,A,3, are obtained.

4. Nitrile-Cleavage Reactions

The $C\equiv N$ bond of acetonitrile or benzonitrile is readily cleaved by $W_2(O-t-Bu)_6$ to form a 1:1 mixture of $W(\equiv CR)(O-t-Bu)_3$ ($R = Me$ or Ph) and the sparingly soluble nitride $W(\equiv N)(O-t-Bu)_3$ (27). The nitride is a one-dimensional coordination polymer $[W(\equiv N)(O-t-Bu)_3]_\infty$ in the solid state (30), resulting from a $W\equiv N \rightarrow W\equiv N \rightarrow W\equiv N$ connectivity. The triple bond in $Me_2NC\equiv N$ is also cleaved by $W_2(O-t-Bu)_6$ to give the nitride polymer and $W(\equiv CNMe_2)(O-t-Bu)_3$ (31), but $Mo_2(O-t-Bu)_6$ (31) and $W_2(OCH_2-t-Bu)_6(HNMe_2)_2$ (32) form only adducts of $Me_2NC\equiv N$, with the ligands side bound through the cyano unit. No carbon–nitrogen cleavage is observed. In an internal competition, the $C\equiv N$ unit of $EtC\equiv C-C\equiv N$ reacts selectively with $W_2(O-t-Bu)_6$ to produce $W(\equiv C-C\equiv CEt)(O-t-Bu)_3(quin)$ (22). This contrasts with the stoichiometric metathesis reaction of $W(\equiv CMe)(O-t-Bu)_3$ and $EtC\equiv C-C\equiv N$, which regioselectively forms $W(\equiv C-C\equiv N)(O-t-Bu)_3(quin)$ (22). Acetonitrile is not cleaved by $W_2[OCMe_2(CF_3)]_6$; an unstable adduct $W_2[OCMe_2(CF_3)]_6(N\equiv CMe)_2$ is formed that loses $MeC\equiv N$ *in vacuo* (24). No reaction is observed between $RC\equiv N$ ($R = \text{alkyl}$) and $Mo_2(O-t-Bu)_6$ (27).

5. Structures

The alkylidyne complexes $W(\equiv CR)(OR')_3$ have either monomeric or dimeric structures depending on the sizes of R and R' . Solution molecular weight measurements show that the bulky $W(\equiv C-t-Bu)(O-t-Bu)_3$ is a monomer (20), and the solid-state structure of $W(\equiv CPh)(O-t-Bu)_3$ comprises pseudotetrahedral molecules with no close intermolecular contacts (33). When the alkylidyne R groups are smaller, e.g., $R = Me$ or Me_2N , weakly associated dimers are found in the solid state, as shown by Fig. 2 (31). The monomeric units of $W(\equiv CNMe_2)(O-t-Bu)_3$ are joined by asymmetric alkoxide bridges (Fig. 2), giving a geometry derived from two trigonal bipyramids sharing an axial–equatorial edge. The bridging alkoxides form dative bonds trans to the alkylidyne ligands, and the W-1–W-2 distance precludes a metal–metal bond. In the solid state, $[W(\equiv CMe)(O-t-Bu)_3]_2$ is isostructural to $[W(\equiv CNMe_2)(O-t-Bu)_3]_2$ (30), and $[W(\equiv CEt)(O-i-Pr)_3(HNMe_2)]_2$ is a closely related edge-sharing bioctahedron (28a). However,

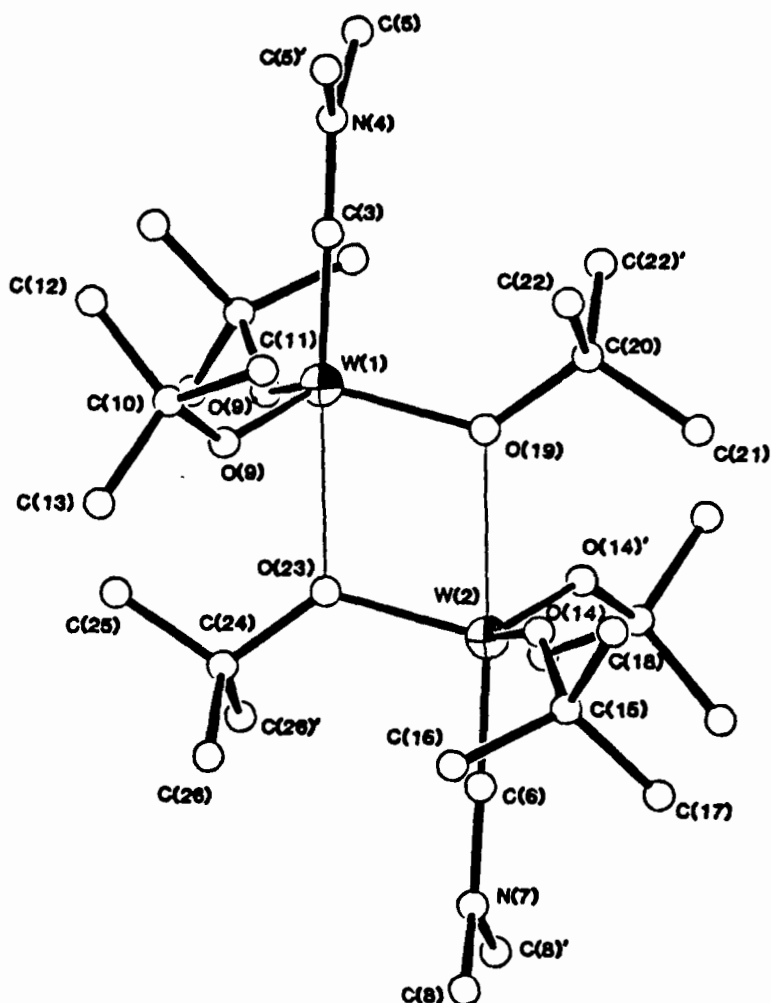


FIG. 2. Ball-and-stick view of $[W(\equiv CNMe_2)(O-t-Bu)_3]_2$ (31). Important bond distances (Å): W-1—O-9 = 1.89(1), W-1—O-19 = 1.95(1), W-1—O-23 = 2.42(1), W-1—C-3 = 1.77(2), and N-4—C-3 = 1.34(2). Reprinted with permission from M. H. Chisholm, J. C. Huffman, and N. S. Marchant, *J. Am. Chem. Soc.* **105**, 6162. Copyright (1983) American Chemical Society (31).

these dimers show ambient temperature NMR spectra consistent with either monomers or rapidly fluxional dimers (22,28a). Low temperature limiting spectra suggest solution-phase dimers (24,34). It seems likely that rapid monomer-dimer equilibria are active at ambient temperature. The methanolysis of $W(\equiv C-t-Bu)(NMe_2)_3$ affords $[W(\equiv C-t-Bu)(OMe)_3]$ -

(HNMe₂)]₂, for which ambient temperature NMR and molecular weight measurements clearly indicate a static, dimeric, solution-phase structure (20). Thus, the smaller alkoxide ligands form stronger bridges between the monomeric units.

B. Reactivity

1. Alkyne Metathesis

a. General Features. The most important aspect of the reactivity of alkylidyne alkoxide complexes is their ability to catalyze the metathesis of alkynes. Schrock found that $W(\equiv C-t-Bu)(O-t-Bu)_3$ will metathesize a variety of internal alkyl and aryl alkynes at significant rates, which are first order in both tungsten and alkyne (21,22). For example, 20 equiv 3-heptyne reaches the equilibrium distribution of 3-hexyne:3-heptyne:4-octyne (1:2:1) in less than 5 minutes and proceeds readily in the presence of acetonitrile, ethyl acetate, phenol, or triethylamine. The complex also catalyzes the metathesis of $EtC\equiv CCH_2NMe_2$, and the cross-metathesis of 3-hexyne and $Me_3SiOCH_2C\equiv CCH_2OSiMe_3$. Hence, considerable functional group tolerance is expected. Terminal alkynes are *not* metathesized by $W(\equiv C-t-Bu)(O-t-Bu)_3$, nor by any other known complex (see Section IV,A,3).

The complexes $W(\equiv CR)(O-t-Bu)_3$ are alkyne metathesis catalysts in general, with activities that depend on R and reaction conditions (22). Several are at least as active as $W(\equiv C-t-Bu)(O-t-Bu)_3$: R = $SiMe_3$, $CH(OEt)_2$, NMe_2 , and $SCMe_3$. The fluoroalkoxide complexes $W(\equiv CR)(OR_F)_3(dme)$ are also active catalysts, but do not exist as $W\equiv CR$ species in the resting state. The reactions of $W(\equiv CR)(OR_F)_3(dme)_n$ with alkynes provide important information about the mechanism of alkyne metathesis and will be covered in Sections IV,A,2,a and IV,B,1. Complex $W(\equiv C-t-Bu)[N(i-Pr)_2]_3$ will also catalyze the reaction (21), but otherwise, alkyne metathesis is limited to alkoxide complexes.

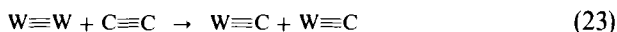
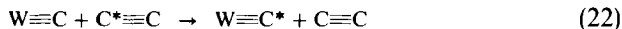
Classic, homogeneous, alkyne metathesis catalysts contain molybdenum, not tungsten (26). Hence, the Schrock group wished to establish that molybdenum(VI) alkylidyne complexes would metathesize alkynes. In contrast to tungsten, $Mo(\equiv C-t-Bu)(O-t-Bu)_3$ will *not* react with internal alkynes (25,26). Complexes $Mo(\equiv C-t-Bu)(O-i-Pr)_3$ and $Mo(\equiv C-t-Bu)(OCH_2-t-Bu)_3$ give only polymerization. However, the fluoroalkoxide complexes $Mo(\equiv C-t-Bu)(OR_F)_3(dme)_n$ do catalyze alkyne metathesis and are in some cases as active as the tungsten compounds discussed above (26). Significantly, known homogeneous catalysts based on molybdenum include phenols or fluoroalcohols in the catalyst recipes (26).

b. Electronic Considerations. Metathesis rates for $W(\equiv CR)(O-t-Bu)_3$ are increased by electron-releasing R groups and decreased by electron-withdrawing R groups (22). Additionally, the rates for electron-rich alkynes such as 3-heptyne are two orders of magnitude faster than for electron-poor alkynes like $p-CH_3C_6H_4C\equiv CPh$ (21). Similar results are obtained for $Mo(\equiv C-t-Bu)[OCMe(CF_3)_2]_3$ (26). These data suggest that the catalyst is electrophilic, and that its alkylidyne ligand is polarized as $M^+ \equiv CR^-$ (22). It also appears that the molybdenum alkylidynes are *less* electrophilic than their tungsten relatives. For example, $Mo(\equiv C-t-Bu)(O-i-Pr)_3$ and $Mo(\equiv C-t-Bu)(OCH_2-t-Bu)_3$ are monomers whereas the tungsten analogs are dimers (26). The *dme* ligand in $W(\equiv C-t-Bu)[OCMe(CF_3)_2]_3(dme)$ is tightly bound whereas $Mo(\equiv C-t-Bu)[OCMe(CF_3)_2]_3$ sublimes base free (26). Schrock *et al.* ascribe the failure of $Mo(\equiv C-t-Bu)(O-t-Bu)_3$ as a metathesis catalyst to the lower electrophilicity of molybdenum relative to tungsten in these compounds. The exchange of alkoxide ligands with fluoroalkoxide ligands compensates for the inherently lower electrophilicity, and imparts catalytic activity to the complexes $Mo(\equiv C-t-Bu)(OR_F)_3(dme)_n$ (26).

At first glance, the characterization of tungsten as more *electrophilic* than molybdenum is an apparent contradiction to the generally held notion that transition metal *basicity* increases on descending a series (35,36). Yet, other observations regarding alkoxide complexes support Schrock's assignment. For example, the Eq. (1) (Section I) equilibria between $M_2(OR)_6$ and the bis-ligand adducts $M_2(OR)_6L_2$ always lie farther toward the latter for $M = W$ versus $M = Mo$ (1). We believe that the greater electrophilic character of tungsten alkoxides can be traced to orbital energetics. Tungsten atomic orbitals are higher lying than those of molybdenum and so have a greater energy separation from oxygen atomic orbitals. As a consequence, tungsten-alkoxide bonds are more polarized as $W^+ - OR^-$. Additionally, third row metals tend to make stronger bonds to ligands, which will also tip Eq. (1) equilibria to the right, causing tungsten to behave as the more electrophilic element, i.e., more Lewis acidic.

At the same time, tungsten alkoxides are better able to donate electron density into ligand π -acceptor orbitals. Hence, tungsten is more π *basic* than molybdenum. The enhanced π basicity also results from orbital energetics; since occupied tungsten orbitals are higher lying they are a better energy match for ligand acceptors. This is clearly indicated by structural, spectroscopic, and theoretical studies of CO adducts of $M_2(OR)_6$ ($M = Mo, W$) which are discussed in Section VIII. We believe it most correct to consider tungsten alkoxides to be more Lewis *acidic* and more π *basic* than their molybdenum counterparts, and that both of these characteristics are likely important to alkyne metathesis activity.

c. *Comparing Alkyne Metathesis and Alkyne Cleavage Reactions.* The metathesis reaction of Eq. (22) and the cleavage reaction of Eq. (23) are clearly conceptually related. Both are metathesis-type reactions. The similarity is reinforced by the observation that $W(\equiv CR)(O-t-Bu)_3$ will metathesize internal alkynes and $W_2(O-t-Bu)_6$ will cleave internal alkynes, while $Mo(\equiv CR)(O-t-Bu)_3$ and $Mo_2(O-t-Bu)_6$ will not, respectively. However, it is important to recognize that Eq. (22) and Eq. (23) are distinct processes,



and that direct analogies do not always exist. For example, $PhC\equiv CPh$ can be metathesized by $W(\equiv C-t-Bu)(O-t-Bu)_3$ (21), but *cannot* be cleaved by $W_2(O-t-Bu)_6$ under normal conditions (22). On the other hand, $W_2(O-i-Pr)_6(HNMe_2)_2$ will cleave 3-hexyne (24,28), but $W(\equiv CEt)(O-i-Pr)_3$ will not metathesize internal alkynes (22,24). Probably the most significant difference in behavior between Eq. (22) and Eq. (23) is that alkyne metathesis is hindered by the presence of Lewis bases such as pyridine or quinuclidine whereas alkyne cleavage is facilitated (22).

2. Coordination of Lewis Bases

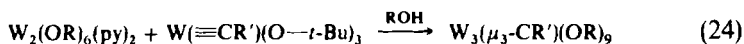
As mentioned several times above, Lewis bases are often necessary components in the syntheses of alkylidyne alkoxide complexes. The adducts $W(\equiv CR')(OR)_3L$ ($R = t-Bu$ and $i-Pr$) are common, and are readily prepared from $W(\equiv CR')(OR)_3$ and pyridine or quinuclidine (22,24). They have a trigonal-bipyramidal geometry, with L and alkylidyne ligands adopting trans axial positions. This is consistent with the solid-state structures of the dimers $[W(\equiv CMe)(O-t-Bu)_3]_2$ (30) and $[W(\equiv CNMe_2)(O-t-Bu)_3]_2$ (31) in which the alkoxide bridges occupy axial positions, trans to $(\equiv CR')$ (see Fig. 2). Recall that the *alkylidene* complexes $W(=CRR')(OCH_2-t-Bu)_2X_2$ coordinate Lewis bases trans to the alkylidene ligand (Section II,B,2) and that the solid-state structure of $W[\overline{=C(CH_2)_3CH_2}](OCH_2-t-Bu)_2Br_2$ (Fig. 1) contains a bridging dative interaction trans to $[\overline{=C(CH_2)_3CH_2}]$. Thus, alkylidene and alkylidyne ligands in alkoxide complexes appear to direct Lewis bases into trans positions. However, it is actually the strongly π -donating alkoxide ligands that are responsible for the observed geometries; coordination of L cis to the alkylidene or alkylidyne would sacrifice an $O \rightarrow W$ bond (30).

The more electrophilic fluoroalkoxide complexes $W(\equiv CR')(OR_F)_3(dme)_n$ react with Lewis bases to form octahedral, bis-ligand adducts $W(\equiv CR')-(OR_F)_3(L)_2$, with OR_F ligands in a mer arrangement (23). As above, one L

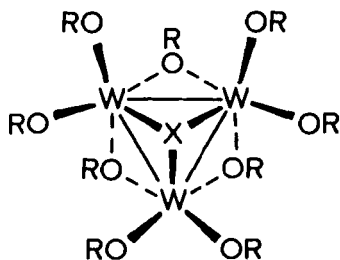
is trans to ($\equiv\text{CR}'$), but the second L coordinates cis to ($\equiv\text{CR}'$). These results may be relevant to the catalysis of alkyne metathesis. The metathesis reaction might reasonably require a cis relationship of alkyne and alkyldiyne ligands; this could be achieved by isomerization of a five-coordinate trans alkyne adduct or by formation of an octahedral bis-alkyne adduct. As will be discussed in Section IV,B,1, evidence in hand suggests that both of these possibilities are operative.

3. Comproportionation Reactions

Combination of the functionalities $\text{M}\equiv\text{M} + \text{C}\equiv\text{C}$ results in the alkyne cleavage reaction [Eq. (23)]. The $\text{M}\equiv\text{C} + \text{C}\equiv\text{C}$ combination gives alkyne metathesis [Eq. (22)]. Another combination, $\text{M}\equiv\text{M} + \text{M}\equiv\text{C}$, was examined by the Chisholm group and was found to give comproportionation chemistry. The reaction between $\text{W}_2(\text{O}-i\text{-Pr})_6(\text{py})_2$ and $\text{W}(\equiv\text{CMe})(\text{O}-t\text{-Bu})_3$ in the presence of *i*-PrOH proceeds according to Eq. (24) (37). The $\text{W}_3(\mu_3\text{-CMe})$ -



$(\text{O}-i\text{-Pr})_9$ product has a structure based on a $\text{W}_3(\mu_3\text{-CMe})$ trimetalla-tetrahedron, as shown by 2. A similar reaction between $\text{Mo}_2(\text{O}-i\text{-Pr})_6$ and $\text{W}(\equiv\text{CMe})(\text{O}-t\text{-Bu})_3$ affords the mixed-metal cluster $\text{Mo}_2\text{W}(\mu_3\text{-CMe})$ -



2

$(\text{O}-i\text{-Pr})_9$ (37). Equation (24) is also successful for $\text{R} = \text{CH}_2-t\text{-Bu}$ and $\text{R}' = \text{Me}$ and Et (38).

4. Hydrolysis Chemistry

Schrock has reported that $\text{W}(\equiv\text{C}-t\text{-Bu})(\text{O}-t\text{-Bu})_3$ reacts with 1 equiv $[\text{Et}_4\text{N}][\text{OH}]$ in aqueous solution to give the oxo alkyl anion $[\text{NEt}_4]^+-$

$[W(CH_2-t-Bu)(=O)_3]^-$, which is stable to air in solution or the solid state for several days (39,40). The related compound $[NEt_4]^+[W(CH_2SiMe_3)(=O)_3]^-$ is prepared similarly, but alkylidyne complexes with β -hydrogens, such as $W(\equiv CET)(O-t-Bu)_3$, are not hydrolyzed cleanly (40). In Section II,A,5 protonation reactions of $W(\equiv C-t-Bu)(O-t-Bu)_3$ were discussed that lead to tungsten alkylidene complexes. Presumably, tungsten alkylidene species are intermediates in the formation of the oxo alkyl anions.

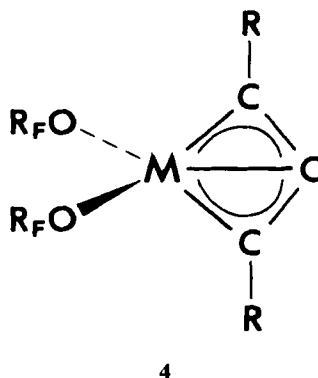
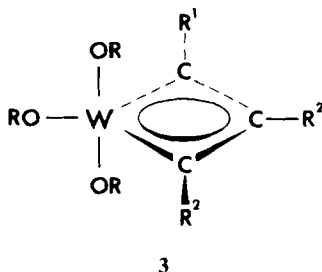
IV

METALLACYCLOBUTADIENE COMPLEXES

A. Synthesis and Properties

1. Preliminary Remarks

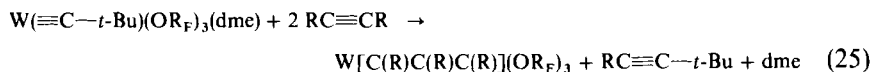
The alkyne metathesis reactions catalyzed by $W(\equiv CR)(O-t-Bu)_3$ are associative in alkyne, suggesting species such as alkylidyne alkyne complexes, metallatetrahedranes, or metallacyclobutadiene complexes as possible intermediates. However, no intermediates are isolable or even detectable in $W(\equiv CR)(O-t-Bu)_3$ systems (22,41). In a search for new catalysts and systems that reveal the nature of intermediates, Schrock and co-workers discovered tungstenacyclobutadiene alkoxide complexes $W[\overline{C(R^1)C(R^2)C(R^2)}](OR)_3$ (3), some of which are active in alkyne metathesis (23,41). Related studies by Schrock *et al.* provided *deprotio* metallacyclobutadiene fluoroalkoxide complexes $M[C_3R_2](OR_F)_2$ (4) ($M = Mo, W$) (26). Taken together, the chemistry of these compounds gives important information regarding



the mechanism of alkyne metathesis, the present lack of catalysts able to metathesize terminal alkynes, the special character of fluoroalkoxide ligands, and events that can lead to alkyne polymerization and catalyst deactivation.

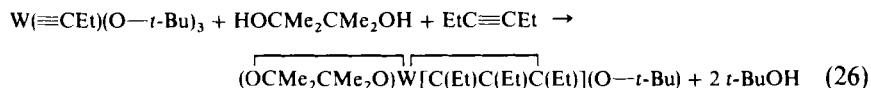
2. Tungstenacyclobutadiene Complexes

a. Preparation from Alkylidyne Complexes. In contrast to $W(\equiv CR)(O-t-Bu)_3$, fluoroalkoxide complexes $W(\equiv C-t-Bu)(OR_F)_3(dme)$ react with an excess of alkyne to yield metallacyclobutadiene complexes according to Eq. (25) (23). The reaction requires both an alkyne-addition step and a metathesis step; when $R_F = CH(CF_3)_2$ and $R = Et$ the initially formed



$W[\overline{C(t-Bu)C(Et)C(Et)}][OCH(CF_3)_2]_3$ is observed. With the bulkier fluoroalkoxide $R_F = CMe(CF_3)_2$ and 2-butyne, a large excess (20 equiv) of alkyne is necessary to achieve Eq. (25) chemistry. Smaller amounts of 2-butyne give only the alkylidyne complex $W(\equiv CMe)[OCMe(CF_3)_2]_3(dme)$. For 3-hexyne Eq. (25) fails completely; even with 40 equiv of alkyne only the alkylidyne complex $W(\equiv CEt)[OCMe(CF_3)_2]_3(dme)$ can be isolated. However, the desired compound $W[\overline{C(Et)C(Et)C(Et)}][OCMe(CF_3)_2]_3$ can be obtained from an exchange reaction between $W[\overline{C(Me)C(Me)C(Me)}][OCMe(CF_3)_2]_3$ and 3-hexyne, which proceeds via $W(\equiv CMe)[OCMe(CF_3)_2]_3$ (in the absence of dme). Apparently, 3-hexyne cannot compete with dme for coordination to the tungsten center.

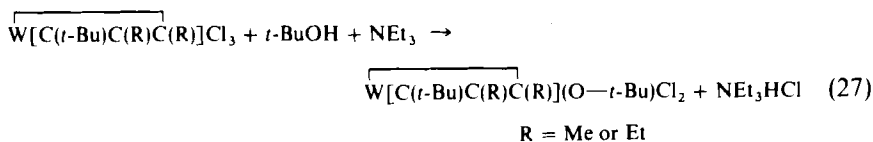
A tungstenacyclobutadiene complex has also been prepared according to Eq. (26) (42,43). Since a similar reaction with pinacol in the absence of 3-



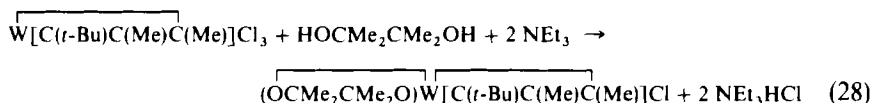
hexyne takes a different course, Schrock proposes that small, undetectable, equilibrium quantities of $W[\overline{C(Et)C(Et)C(Et)}](O-t-Bu)_3$ are trapped by pinacol in Eq. (26).

b. Preparation from Halide Complexes. The useful precursors $W[\overline{C(t-Bu)C(R)C(R)}]Cl_3$ are easily prepared from $W(\equiv C-t-Bu)Cl_3(dme)$ and $RC\equiv CR$ (42,43). Subsequent conversion to alkoxide complexes is ac-

complished by Eq. (27). When $\text{LiO}-t\text{-Bu}$ is added to $\text{W}[\text{C}(t\text{-Bu})\text{C}(\text{R})\text{C}(\text{R})](\text{O}-t\text{-Bu})\text{Cl}_2$, only $\text{W}(\equiv\text{CR})(\text{O}-t\text{-Bu})_3$ complexes are formed ($\text{R} = \text{Me}$,



Et , or $t\text{-Bu}$), confirming the instability of $\text{W}[\text{C}(\text{R})\text{C}(\text{R}')\text{C}(\text{R}')](\text{O}-t\text{-Bu})_3$ species. A pinacolato derivative is obtained as shown in Eq. (28). Re-



action of $(\text{OCMe}_2\text{CMe}_2\text{O})\text{W}[\text{C}(t\text{-Bu})\text{C}(\text{Me})\text{C}(\text{Me})]\text{Cl}$ with $\text{LiO}-t\text{-Bu}$ provides $(\text{OCMe}_2\text{CMe}_2\text{O})\text{W}[\text{C}(t\text{-Bu})\text{C}(\text{Me})\text{C}(\text{Me})](\text{O}-t\text{-Bu})$, a compound analogous to the product of Eq. (26). All of the tungstenacyclobutadiene complexes described here are thought to have structures similar to **3** (see above), with chloride or pinacolato ligands substituted for OR where appropriate.

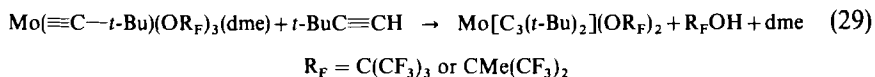
c. Stability of Metallacyclobutadiene Complexes. Metallacyclobutadiene complexes are fairly labile species. For example, pyridine readily displaces alkyne from $\text{W}[\text{C}(\text{Et})\text{C}(\text{Et})\text{C}(\text{Et})][\text{OCH}(\text{CF}_3)_2]_3$ to give $\text{W}(\equiv\text{CEt})[\text{OCH}(\text{CF}_3)_2]_3(\text{py})_2$ (23). Also the inability of 3-hexyne to compete with the stronger donor dme for coordination to $\text{W}(\equiv\text{CEt})[\text{OCMe}(\text{CF}_3)_2]_3$ was noted above. Thus, metallacyclobutadiene complexes seem to behave as weak, Lewis base adducts of alkylidyne complexes. These data suggest a significant electronic component to stability; an increase in electrophilicity at tungsten should result in stronger alkyne binding and increase the stability of metallacyclobutadiene complexes. Hence, the fluoroalkoxide complexes $\text{W}[\text{C}(\text{R})\text{C}(\text{R})\text{C}(\text{R})](\text{OR}_\text{F})_3$ are isolable, but the corresponding compounds with the electron-releasing *tert*-butoxide ligands are not detectable. Despite the several examples of tungstenacyclobutadiene alkoxide complexes, no stable examples of molybdenacyclobutadiene alkoxide complexes are known (26), consistent with the lower electrophilicity of molybdenum alkoxides relative to tungsten alkoxides (see Section III,B,1,b).

Why is it that the pinacolato derivatives $(\text{OCMe}_2\text{CMe}_2\text{O})\text{W}[\text{C}(\text{R})\text{C}(\text{R}')\text{C}(\text{R}')](\text{O}-t\text{-Bu})$ are stable? The pinacolato ligand is less effective at π donation than two *tert*-butoxide ligands, and is thus

a comparatively poor electron donor for two reasons: the $\overbrace{\text{W}-\text{O}-\text{C}-\text{C}-\text{O}}$ ring (1) constrains the W—O—C angles, and (2) also restricts conformation of the W—O bonds about the W atom. Both factors limit the formation of strong O → W π bonds. However, the pinacolato ligand is not the *steric* equivalent of two *tert*-butoxides either, and a steric component to the stability of metallacyclobutadiene complexes should be recognized. This is apparent in the relative stabilities of the complexes supported by $\text{OCH}(\text{CF}_3)_2$ versus $\text{OCMe}(\text{CF}_3)_2$ ligands (23). Although the ligands should be electronically fairly similar, the tungstenacyclobutadiene complexes derived from the latter, bulkier fluoroalkoxide are much less stable.

3. Deprotio Metallacyclobutadiene Complexes

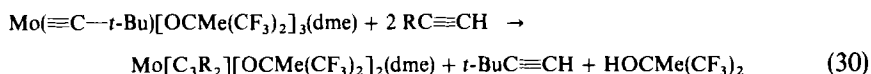
As described in Section III,A,3, $\text{Mo}(\equiv\text{C}-t\text{-Bu})(\text{O}-t\text{-Bu})_3$ reacts with terminal alkynes to give new alkylidyne complexes by a stoichiometric metathesis process. However, different chemistry is generally found with fluoroalkoxide complexes $\text{Mo}(\equiv\text{C}-t\text{-Bu})(\text{OR}_F)_3(\text{dme})_n$ and terminal alkynes that yields deprotio molybdenacyclobutadiene complexes according to Eq. (29) (26). The metallacyclic products are assigned pseudotetrahedral



geometries as shown by **4** (see above). A reasonable mechanism for their formation is elimination of R_FOH from intermediate metallacyclobutadiene complexes $\text{Mo}[\text{C}(t\text{-Bu})\text{C}(\text{H})\text{C}(t\text{-Bu})](\text{OR}_F)_3$. Results consistent with this proposal are presented below.

The deprotio molybdenacyclobutadiene complexes form Lewis base adducts. For example, addition of pyridine to $\text{Mo}[\text{C}_3(t\text{-Bu})_2][\text{OCMe}(\text{CF}_3)_2]_2$ gives the octahedral bis-pyridine adduct $\text{Mo}[\text{C}_3(t\text{-Bu})_2][\text{OCMe}(\text{CF}_3)_2]_2(\text{py})_2$ (26). In some cases the presence of a Lewis base is necessary to achieve chemistry similar to Eq. (29); thus, $\text{Mo}(\equiv\text{C}-t\text{-Bu})[\text{OCH}(\text{CF}_3)_2]_3(\text{dme})$, $t\text{-BuC}\equiv\text{CH}$, and pyridine give $\text{Mo}[\text{C}_3(t\text{-Bu})_2][\text{OCH}(\text{CF}_3)_2]_2(\text{py})_2$. In the absence of pyridine, the metallacycle reacts further with alkyne (see Section IV,B,3).

The alkylidyne complex $\text{Mo}(\equiv\text{C}-t\text{-Bu})[\text{OCMe}(\text{CF}_3)_2]_3(\text{dme})$ reacts with smaller alkynes according to Eq. (30). This suggests that the proposed



$\text{R} = n\text{-Pr}, i\text{-Pr}, \text{ or Ph}$

intermediate $\text{Mo}[\text{C}(t\text{-Bu})\text{C}(\text{H})\text{C}(\text{R})](\text{OR}_F)_3$ loses $t\text{-BuC}\equiv\text{CH}$ and adds $\text{RC}\equiv\text{CH}$ in a metathesis process faster than it eliminates R_FOH .

The reactivity of systems supported by the fluoroalkoxide $\text{OCMe}_2(\text{CF}_3)$ is more complicated. Terminal alkynes $\text{RC}\equiv\text{CH}$ and $\text{Mo}(\equiv\text{C}-t\text{-Bu})[\text{OCMe}_2(\text{CF}_3)]_3$ give only new $\text{Mo}\equiv\text{CR}$ alkylidyne complexes by metathesis unless a Lewis base is present. With pyridine, the deprotio molybdenacyclobutadiene complexes $\text{Mo}[\text{C}_3\text{R}_2][\text{OCMe}_2(\text{CF}_3)]_2(\text{py})_2$ are then formed. The Lewis base does more than trap the metallacycle as an adduct; a similar procedure using quinuclidine leads to the *base-free* product $\text{Mo}[\text{C}_3(t\text{-Bu})_2][\text{OCMe}_2(\text{CF}_3)]_2$. It is likely that added base catalyzes R_FOH elimination by deprotonation of the $\text{C}_\beta\text{-H}$ in the $\text{Mo}[\text{C}(t\text{-Bu})\text{C}(\text{H})\text{C}(t\text{-Bu})](\text{OR}_F)_3$ intermediate.

Schrock's group has prepared analogous deprotio tungstenacyclobutadiene complexes from tungsten alkylidynes and terminal alkynes (26,44a,44b). In contrast to the molybdenum chemistry above, the intermediate tungstenacyclobutadiene complexes $\text{W}[\text{C}(\text{R})\text{C}(\text{H})\text{C}(\text{R}')][\text{OCH}(\text{CF}_3)_2]_3$ are in some cases isolable and are converted to deprotio tungstenacyclobutadiene complexes in the presence of Lewis bases (44b). Thus, $\text{W}[\text{C}(t\text{-Bu})\text{C}(\text{H})\text{C}(t\text{-Bu})][\text{OCH}(\text{CF}_3)_2]_3$ and pyridine react to give $\text{W}[\text{C}_3(t\text{-Bu})_2][\text{OCH}(\text{CF}_3)_2]_2(\text{py})_2$.

The results above provide a strong rationalization for the present lack of catalysts able to metathesize *terminal* alkynes (26). The ready elimination of alcohol to form deprotio metallacyclobutadiene complexes obviously alters the character of the catalyst. This can lead to deactivation or can introduce new modes of reactivity that interfere with the metathesis reaction (see Section IV,B,3).

4. Structures

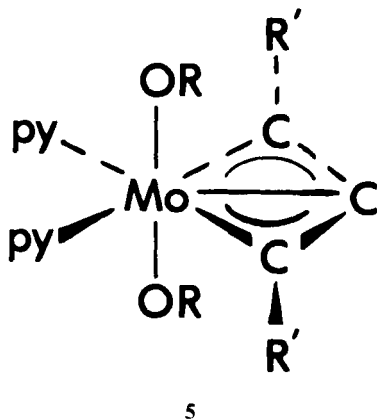
Several of the metallacyclic compounds have been characterized by X-ray crystallography, confirming proposed geometries and providing insights into the function of supporting ligands and the nature of catalytic intermediates.

As expected, $\text{W}[\text{C}(\text{Et})\text{C}(\text{Et})\text{C}(\text{Et})][\text{OCH}(\text{CF}_3)_2]_3$ has a trigonal-bipyramidal structure based on **3** (see above) (23). The metallacyclobutadiene ring is planar, and lies in the equatorial plane. Although Schrock has found several different geometries for $\text{M}(\text{CR})_3$ units in related complexes, only trigonal-bipyramidal compounds with planar $\text{M}(\text{CR})_3$ rings can metathesize alkynes (13a,22), suggesting this special case represents a true catalytic intermediate.

The structural parameters for the fluoroalkoxide ligands are also revealing. In contrast to the short $\text{W}-\text{O}$ distances [1.816–1.828(4) Å] and large $\text{W}-\text{O}-\text{C}$ angles [145.4–145.6(4)°] found for the alkoxide ligands in $\text{W}[\text{C}(\text{CH}_2)_3\text{CH}_2](\text{OCH}_2-t\text{-Bu})_2\text{Br}_2$ (see Section II,A,4), the

$\text{OCH}(\text{CF}_3)_2$ ligands show long W—O distances of 1.932–1.982(11) Å and small W—O—C angles of 129.4–138.6(10)° (23). These data reflect the lessened π -donor ability of fluoroalkoxide ligands due to the electron-withdrawing CF_3 groups that is responsible for the greater electrophilic character of fluoroalkoxide complexes relative to alkoxide complexes. In electronic terms, fluoroalkoxides more closely resemble halides; they are poor π -donor, electronegative ligands. But in steric terms, the fluoroalkoxides are much larger than the small halides. The combination of steric bulk and electronegative character distinguishes the fluoroalkoxides (and aryloxides) from other uninegative ligands.

The pseudooctahedral structure determined for $\text{Mo}[\text{C}_3(t\text{-Bu})_2][\text{OCH}(\text{CF}_3)_2]_2(\text{py})_2$ is depicted by **5** (26). Like the tungstenacycle, the $\text{Mo}(\text{C}_3\text{R}_2)$



unit is planar. The Mo—C_β distance is quite short, 2.005(4) Å, barely longer than the Mo—C_α distance, 1.943(3) Å. As with alkylidene alkoxide and alkylidyne alkoxide complexes, the Lewis bases coordinate trans to the carbon ligand (see Section III,B,2). These observations along with others to follow (see Sections VI,A,3 and VIII,A,2) suggest an empirical rule for organometallic molybdenum and tungsten alkoxides, that neutral σ -donor ligands will generally prefer to coordinate trans to carbon ligands rather than trans to alkoxides. There are some exceptions (see Section V,A,2).

B. Reactivity

1. Alkyne Metathesis

The most significant aspect of tungstenacyclobutadiene chemistry is the prospect that the compounds are intermediates in catalytic alkyne metathesis. Schrock's discovery of tungstenacyclobutadiene complexes that are them-

selves metathesis catalysts is therefore of great importance to the study of mechanism. Reaction kinetics and activation parameters for these systems allow several conclusions to be reached.

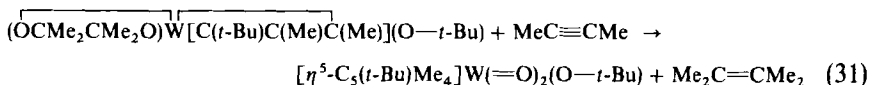
Although this article is concerned with alkoxide chemistry, Schrock's findings in a closely related aryloxide area are necessary for a complete perspective. The complexes $\overline{W[C(R)C(R)C(R)]}[O-2,6-C_6H_3(i-Pr)_2]_3$ ($R = Et$ or $n-Pr$) are slow metathesis catalysts, producing an equilibrium alkyne distribution from 20 equiv 3-heptyne with a $t_{1/2}$ of 4.5 hours (41). Variable temperature kinetic studies of the incorporation of 3-hexyne- d_{10} into the compounds give activation parameters $\Delta H^\ddagger = +26.1(4)$ kcal/mol and $\Delta S^\ddagger = +15.2(15)$ eu for $R = Et$. The reactions are first order in tungstenacycle and zero order in 3-hexyne- d_{10} . These results fit a mechanism in which loss of alkyne from the tungstenacyclobutadiene to generate an alkylidyne complex is the rate-determining step (41). Then complexation of alkyne to the alkylidyne complex would initiate the next catalytic cycle. Studies with the fluoro-alkoxide complexes $\overline{W[C(R)C(R)C(R)]}[OCMe(CF_3)_2]_3$ ($R = Me$ or Et) give qualitatively similar results, but the reactions are much faster (23). Therefore, trigonal-bipyramidal tungstenacyclobutadiene complexes appear to be the significant intermediates in several alkyne metathesis systems, consistent with expectation.

But not all systems behave in this way. Incorporation of 3-hexyne- d_{10} into $\overline{W[C(Et)C(Et)C(Et)]}[OCH(CF_3)_2]_3$ is first order in tungstenacycle and *first order* in 3-hexyne- d_{10} (23). Variable temperature kinetics yield the activation parameters $\Delta H^\ddagger = +14.4(6)$ kcal/mol and $\Delta S^\ddagger = -22.8(20)$ eu. These data require a bimolecular reaction between tungstenacyclobutadiene and alkyne. The complex is a fairly rapid alkyne metathesis catalyst (23); apparently, the metathesis reaction is in this case *associative* in alkyne, proceeding through an intermediate containing the equivalent of alkylidyne complex plus two alkynes. On the basis of observed geometries for Lewis base adducts of alkylidyne alkoxide complexes, we suggested (in Section III,B,2) that alkyne metathesis might proceed by *either* five-coordinate "mono-alkyne" adducts (i.e., metallacyclobutadiene complexes) or six-coordinate "bis-alkyne" adducts. The kinetic evidence presented here is consistent with our analogy. At present it is unclear what factors select between associative and dissociative mechanisms, but the electronic similarity of $OCH(CF_3)_2$ and $OCMe(CF_3)_2$ suggest that steric effects may be important (23). The structure of the "bis-alkyne, alkylidyne" intermediate is also unknown.

2. Cyclopentadienyl Ligand Formation

Tungstenacyclobutadiene complexes with halide or pinacolato ligands are not alkyne metathesis catalysts. However, they do react with alkynes in

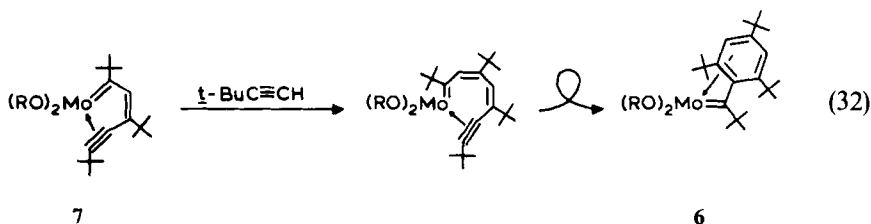
certain cases to give η^5 -cyclopentadienyl complexes, as shown by the example in Eq. (31) (42,43). This strategy has proven synthetically useful in



the preparation of homo- and heterobimetallic complexes with linked η^5 -cyclopentadienyl ligands (45). It is interesting to note that the η^5 -cyclopentadienyl complexes have the same alkyne-alkylidyne stoichiometry as the higher order metathesis intermediate discussed above. We can speculate that they might form from the same species, such as a metallabenzene (43). Cyclopentadienyl formation should also be considered a reasonable mechanism for alkyne metathesis catalyst deactivation (42).

3. Deprotio Molybdenacyclobutadiene Ring Expansion

Reaction of $\text{Mo}[\text{C}_3(t\text{-Bu})_2][\text{OCH}(\text{CF}_3)_2]_2(\text{py})_2$ with excess $t\text{-BuC}\equiv\text{CH}$ at 40°C gives a product of empirical formula $\text{Mo}[\text{C}_7\text{H}_2(t\text{-Bu})_4][\text{OCH}(\text{CF}_3)_2]_2$ (46). The product is best prepared from $\text{Mo}(\equiv\text{C}-t\text{-Bu})[\text{OCH}(\text{CF}_3)_2]_3(\text{dme})$ and $t\text{-BuC}\equiv\text{CH}$ in the absence of pyridine (see Section IV, A, 3). Spectroscopic data and a crystallographic study of a suitable derivative indicate that the compound is an alkylidene complex with a π -bound arene ring as shown by **6** [Eq. (32)]. Closer examination reveals an intermediate in the formation of **6** that can be isolated and structurally characterized as the metallacycle **7** [Eq. (32)], resulting from the addition of a single equivalent of $t\text{-BuC}\equiv\text{CH}$ to the deprotio molybdenacyclobutadiene complex (46). Thus, **6** likely forms by two successive ring-enlargement steps followed by a rearrangement (termination step) to yield the observed structure.



Alkyne polymerization frequently competes with alkyne metathesis, especially for complexes with smaller alkoxide ligands (26). The ring-enlargement chemistry above provides a possible model for propagation steps of alkyne polymerization via alkylidene complexes. Katz *et al.* have also proposed that alkynes are polymerized by alkylidene complex contaminants in

alkylidyne systems (47). Several means for generating alkylidene complexes from alkylidyne alkoxides are imaginable, such as protonation by trace acids (see Section II,A,5). Similar ring-expansion chemistry should also be possible from metallabenzene intermediates (46), which might form from alkylidyne complexes and internal alkynes.

Steric effects on polymerization tendencies are easily explained in this context. Small alkoxide ligands allow rings such as **7** to form and to continue to grow without termination until polymer sizes are reached. Large alkoxide ligands would inhibit the initial formation of such rings, allowing alkyne metathesis to proceed undisturbed.

V

DINUCLEAR ALKYNE COMPLEXES

A. Synthesis and Properties

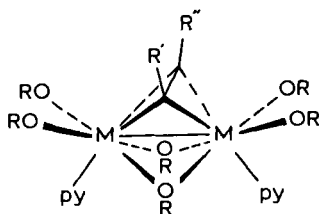
1. Preliminary Remarks

Alkyne adducts are likely intermediates in the alkyne cleavage and alkyne metathesis reactions discussed in Sections III and IV. Few examples of mononuclear alkyne alkoxide complexes are presently known (48). However, an extensive series of dinuclear alkyne alkoxide complexes have been prepared by the Chisholm group. Their studies reveal a complex system of chemical equilibria surrounding these compounds, from which the mechanisms of alkyne cleavage and alkyne oligomerization processes, and the factors that select between the two, can be examined. The differing characters of molybdenum and tungsten alkoxides are also demonstrated and readily justified.

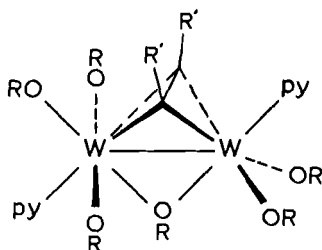
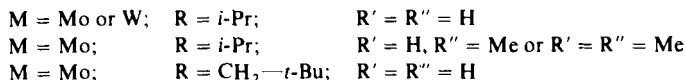
2. Preparation and Structure

Addition of stoichiometric quantities of alkyne to $M_2(OR)_6(py)_2$ or to $M_2(OR)_6$ in the presence of pyridine gives the perpendicular alkyne adducts **8–10** (38,49–52). Spectroscopic and structural data for **8–10** are detailed in a recent review (53).

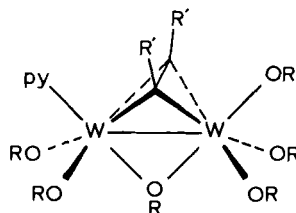
The three observed structures, **8–10**, are based on dimetallatetrahedra in which M—M, M—C, and C—C bond orders are all close to 1. Distinction between the three is apparent in octahedral (oct) versus trigonal-bipyramidal (tbp) geometries for the individual metal centers: **8** is oct–oct, **9** is oct–tbp, and



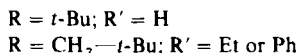
8



9



10



10 is *tbp*-*tbp*. This formalism considers the bridging alkyne to occupy a single coordination site at each metal center. A fairly clear trend of increasing M—M and C—C bond distances is found for **8** through **10** (38,53), suggesting that structure-type **10** is most effective at metal-to-alkyne backbonding and structure-type **8** least effective. The preference for structure type has a steric dependence, with larger R and R' groups progressively favoring **9** and then **10**. Molybdenum alkyne adducts adopt structure **8** only, and structural parameters indicate more extensive metal-to-alkyne backbonding for the tungsten compounds, consistent with the greater π basicity of tungsten alkoxides relative to molybdenum alkoxides (see Sections III,B,1,b, VIII,A,2, and VIII,A,3). Thus, alkynes are bound more tightly in the tungsten complexes; only Mo₂(μ -C₂Me₂)(O-*i*-Pr)₆(py)₂ shows a reversible alkyne dissociation in solution (49,50).

We have proposed an empirical rule for organometallic alkoxide complexes, that Lewis base coordination will prefer the *trans* position to a carbon ligand (see Section IV,A,4). Structures **9** and **10** are among the few examples that *do not* obey this rule. However, we believe the *basis* for the rule is that Lewis bases will coordinate in the way that *least* disrupts alkoxide-to-tungsten π donation,

and this is usually trans to carbon ligands (see Section III,B,2) (30). Exceptions to the rule are found among dinuclear systems, not mononuclear systems, and likely reflect complications due to M—M bonds (especially multiple M—M bonds) and additional possible geometric isomers. In the case of **9** and **10**, theoretical studies indicate that good O → W π bonding is maintained (54). Furthermore, structures **8** and **9** can interconvert, and are probably generally quite close in energy (38). For example, $\text{Mo}_2(\mu\text{-C}_2\text{H}_2)(\text{OCH}_2\text{-}t\text{-Bu})_6(\text{py})_2$ is isolated as **8**, but exists in solution as an approximately 10:1 ratio of **8**:**9**. For $\text{W}_2(\mu\text{-C}_2\text{H}_2)(\text{OCH}_2\text{-}t\text{-Bu})_6(\text{py})_2$, which is isolated as **9**, the situation is reversed. Dynamic exchange, $\mathbf{8} \rightleftharpoons \mathbf{9}$, is evident in variable temperature NMR studies. Thus, the relative energies differ by only about 1 kcal/mol. Although we have no direct evidence that **8** or **9** can interconvert with **10**, we do note that reversible pyridine dissociation from **8** and **9** (and **10**) is facile (38,52).

Cotton has reported a related bis-alkyne dinuclear complex, $\text{W}_2(\mu\text{-C}_2\text{Ph}_2)_2(\text{O-}t\text{-Bu})_4$, that is formed in low yield in the reaction between $\text{W}_2(\text{O-}t\text{-Bu})_6$ and $\text{PhC}\equiv\text{CPh}$ in toluene at 70°C (55). The structure consists of two edge-sharing dimetallatetrahedra, fused along the M—M edge. Bond distances within the dimetallatetrahedra are quite comparable to $\text{W}_2(\mu\text{-C}_2\text{H}_2)(\text{O-}t\text{-Bu})_6(\text{py})$.

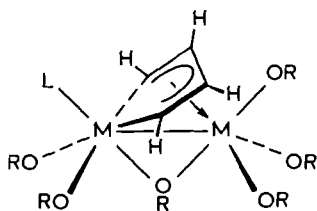
3. Comparing $M_2(\mu\text{-C}_2R'_2)$ to Other $M_x(CR')_{4-x}$ Systems ($x = 1, 2$, or 3)

Three $M_x(CR')_{4-x}$ stoichiometries have now been examined: $M(CR')_3$, i.e., $M\equiv C + C\equiv C$; $M_3(CR')$, i.e., $M\equiv M + M\equiv C$; and $M_2(CR')_2$, i.e., $M\equiv M + C\equiv C$. As discussed extensively in Sections III and IV, alkylidyne *alkoxide* complexes and $R'C\equiv CR'$ give metathesis reactions, never isolable metallatetrahedra $M(CR')_3$. In contrast, reactions of $(\text{RO})_3M\equiv M(\text{OR})_3$ and $(\text{RO})_3M\equiv CR'$ lead to the trimetallatetrahedra $M_3(\mu_3\text{-CR}')$ by disproportionation, never to metathesis products (see Section III,B,3). Thus $\text{Mo}_2(\text{O-}i\text{-Pr})_6$ and $\text{W}(\equiv\text{CMe})(\text{O-}t\text{-Bu})_3$ in the presence of *i*-PrOH give the mixed-metal $\text{Mo}_2\text{W}(\mu_3\text{-CMe})$ cluster, not $(i\text{-Pro})_3\text{Mo}\equiv\text{W}(\text{O-}i\text{-Pr})_3$ and $\text{Mo}(\equiv\text{CMe})(\text{O-}i\text{-Pr})_3$. However, both metathesislike and disproportionation reactivities are found for the intermediate case ($x = 2$), $(\text{RO})_3\text{-M}\equiv\text{M}(\text{OR})_3$ plus $R'C\equiv CR'$. Bulky combinations of R and R' lead to cleavage products $M(\equiv CR')(\text{OR})_3$ (see Section III,A,2); less sterically demanding combinations (in the presence of py) give the dimetallatetrahedra **8–10**. Hence, a clear trend in the stabilities of the tetrahedra (relative to two triply bonded units) is apparent, $M(CR')_3 < M_2(\mu\text{-C}_2R'_2) < M_3(\mu\text{-CR}')$, which can be rationalized to result from the much greater strength of σ versus π bonds for heavier elements (in this case M) (56). As will be shown below, $M_2(\mu\text{-C}_2R'_2)$ dimetallatetrahedra and $M\equiv CR'$ alkylidyne complexes are readily interconvertible.

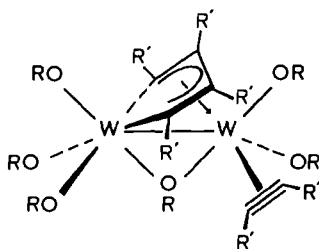
B. Reactivity

1. Alkyne C—C Bond-Forming Reactions

Complexes $M_2(\mu-C_2R'_2)(OR)_6(py)_n$ react with additional $R'C\equiv CR'$ to yield $\mu-C_4R'_4$ adducts of type **11** and **12** (49–51,57). The compounds **11** and **12**

**11**

M = Mo or W, R = CH_2-t-Bu , L = py
M = W, R = $t-Bu$, L = none

**12**

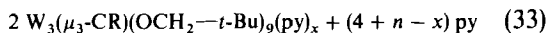
R = $i-Pr$, R' = H, Me, or Et
R = CH_2-t-Bu , R' = H or Me

can also be prepared directly from reactions of $M_2(OR)_6(py)_n$ and 2 or 3 equiv $R'C\equiv CR'$, respectively. For the case of **12** (R = $i-Pr$, R' = Me), the intermediate $W_2(\mu-C_2Me_2)(O-i-Pr)_6(py)_n$ is too unstable to isolate or even detect (57). Labeling studies have shown, for both molybdenum and tungsten compounds, that the $\mu-C_4H_4$ ligand is formed from a simple alkyne-coupling process; C—C or CH scrambling processes are not observed (50,57).

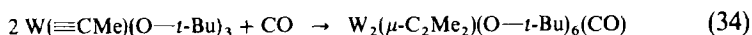
The molybdenum compound $Mo_2(\mu-C_4H_4)(OCH_2-t-Bu)_6(py)$ catalytically transforms C_2H_2 into polyacetylene and benzene (approximately 95:5 ratio, respectively) (50). Labeling studies indicate that the $\mu-C_4H_4$ ligand is incorporated exclusively into the benzene product. Thus, the $\mu-C_4H_4$ complex is involved only in cyclotrimerization. Although not observed for molybdenum, compounds of structure **12** are likely intermediates. Significantly, the tungsten compounds do not catalyze cyclotrimerization, but $W_2(\mu-C_4Me_4)(\mu^2-C_2Me_2)(OR)_6$ complexes thermally decompose to give hexamethylbenzene (57).

2. Evidence for Equilibria $M_2(\mu-C_2R_2) \rightleftharpoons 2 M\equiv CR$

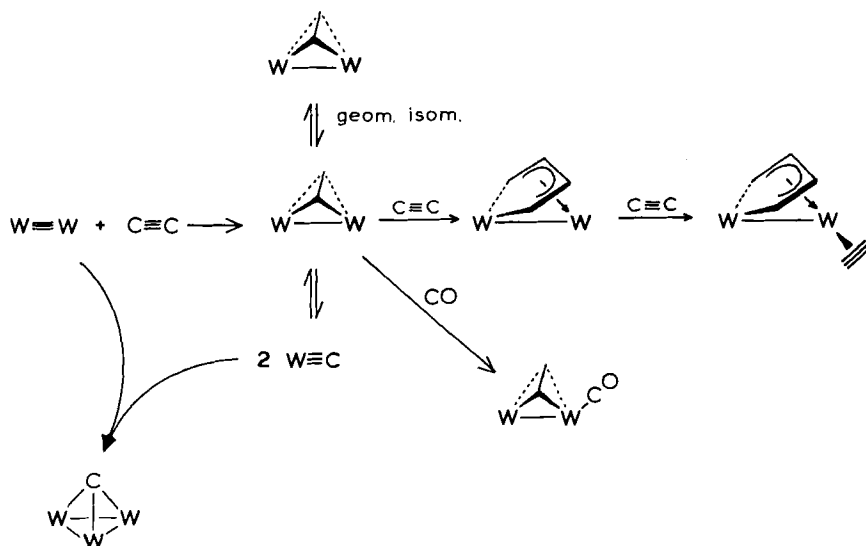
An observable equilibrium between dinuclear alkyne adducts and mononuclear alkylidyne complexes was first suspected when Chisholm and Hoffman detected small amounts ($\sim 20\%$) of $W(\equiv CH)(O-t-Bu)_3$ in the ^{13}C -NMR spectrum of $W_2(\mu-C_2H_2)(O-t-Bu)_6(py)$ (52). They subsequently showed that combination of $W_2(\mu-^*C_2H_2)(O-t-Bu)_6(py)$ and $W_2(\mu-C_2D_2)(O-t-Bu)_6(py)$ leads to the rapid appearance of resonances for the $W_2(\mu-H^*CCD)$

$$W_2(\mu-C_2R_2)(OCH_2-t-Bu)_6(py)_n + 2 W_2(OCH_2-t-Bu)_6(py)_2 \rightarrow$$


Section III,B,3 established that $M \equiv M$ and $M \equiv CR$ units couple to give $M_3(\mu-CR)$ clusters, Eq. (33) implies the trapping of equilibrium quantities of $W(\equiv CR)(OCH_2-t-Bu)_3$ by $W_2(OCH_2-t-Bu)_6(py)_2$. Finally, conversion in the opposite direction, $2 M \equiv CR \rightarrow M_2(\mu-C_2R_2)$, is confirmed by Eq. (34) (58).



The varied reactivity of the alkyne adducts $M_2(\mu-C_2R_2)$ is summarized in Scheme 1. Of principal importance is the interconversion of $M_2(\mu-C_2R_2)$ and $M\equiv CR$, for which the equilibrium partners are either spectroscopically codetectable, or can be trapped in various ways, as described above. Additionally, the $M_2(\mu-C_2R_2)$ complexes are labile to isomerization (e.g.,



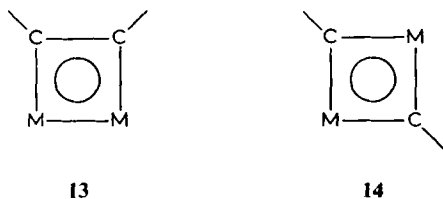
SCHEME 1

$8 \rightleftharpoons 9$, see above) and to C—C bond-forming reactions with alkynes. The direction of the $M_2(\mu-C_2R_2) \rightleftharpoons 2 M \equiv CR$ equilibrium depends on steric effects. No methylidyne complex can be observed in the spectrum of $W_2(\mu-C_2H_2)(OR)_6(py)_2$ for the smaller alkoxides $R = i\text{-Pr}$ or $CH_2-t\text{-Bu}$, and double-labeling experiments (as above) do not give crossover products (38,52). On the other hand, larger alkoxides and alkynes favor the cleavage products $M \equiv CR$ such that the $M_2(\mu-C_2R_2)$ adducts, e.g., $W_2(\mu-C_2Me_2)(O-i\text{-Pr})_6(py)_n$, are not detectable (except by chemical trapping, see above). The complexity of the chemistry outlined in Scheme 1 is demonstrated by the temperature-dependent reactivity of $W_2(O-i\text{-Pr})_6(HNMe_2)_2$ with 3-hexyne (24,28a). Low temperature reactions (-20°C) give cleavage to $[W(\equiv C\text{Et})(O-i\text{-Pr})_3(HNMe_2)]_2$ (see Sections III,A,2 and III,A,5); room temperature reactions give a mixture that contains $W_3(\mu_3-C\text{Et})(O-i\text{-Pr})_9$ and the coupling product $W_2(\mu-C_4Et_4)(\eta^2-C_2Et_2)(O-i\text{-Pr})_6$ (12).

3. Mechanism of Alkyne Cleavage

Several mechanistic questions can be considered. What sequence of steps converts $M_2(OR)_6$ compounds and alkynes to alkylidyne complexes? How do steric effects promote the cleavage reaction? Do electronic or other effects contribute?

The results above suggest one of the first steps is the formation of the dimetallatetrahedra $M_2(\mu-C_2R_2)$. There is no *a priori* reason why these species could not cleave directly to the $M \equiv CR$ products. However, if an intermediate(s) exists between $M_2(\mu-C_2R_2)$ and $2 M \equiv CR$, and no evidence presently requires it, then two possibilities are most likely: 1,2- or 1,3-dimetallacyclobutadiene complexes, **13** or **14** (22,24). Of the two, **14** is



preferable for the reason, among others (22,24), that it corresponds to a step-wise reduction in C—C and M—M bond order (B.O.): $RC \equiv CR$ (B.O. 3) to $M_2(\mu-C_2R_2)$ (B.O. ~ 1) to **14** (B.O. ~ 0). In contrast, the intermediacy of **13** would not correspond to a step-wise bond-order reduction: $RC \equiv CR$ (B.O. 3) to $M_2(\mu-C_2R_2)$ (B.O. ~ 1) to **13** (B.O. ~ 1.5) to $2 M \equiv CR$ (B.O. 0).

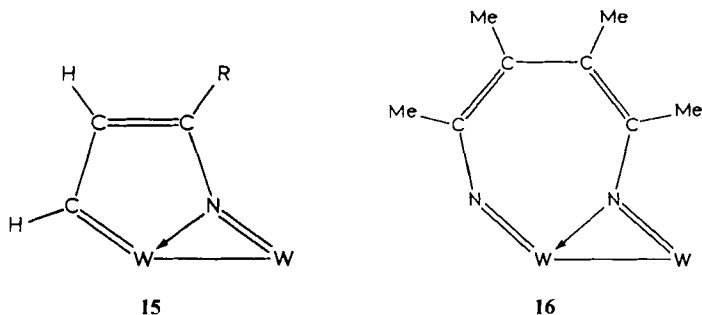
Small alkoxide ligands can inhibit cleavage to intermediate **14** or to end-product $M \equiv CR$ complexes by forming strong $\mu\text{-OR}$ bridges that stabilize the

$M_2(\mu-C_2R_2)$ dimers (see Section III,A,5). Large alkoxides, e.g., *t*-BuO, are poorer bridging ligands and better π -donor terminal ligands, thus promoting cleavage of the $M_2(\mu-C_2R_2)$ moiety (22). Steric bulk also limits the access of excess alkyne to the metal center, preventing C—C bond-forming oligomerization (see Scheme 1) (22). Lewis bases assist the cleavage reaction probably by impeding the recombination of $2 M\equiv CR$ to give $M_2(\mu-C_2R_2)$ (22). Lewis bases may also stabilize $(M)^{6+}$ relative to $(M)^{5+}$ in the $M\equiv CR$ and $M_2(\mu-C_2R_2)$ compounds, respectively.

Alkyne cleavage can be viewed as a ligand reduction process that converts $RC\equiv CR$ to two $(CR)^{3-}$ ligands, and a $(M\equiv M)^{6+}$ center to two $(M)^{6+}$ fragments. The $(W\equiv W)^{6+}$ unit is more easily oxidized than the $(Mo\equiv Mo)^{6+}$ unit and consequently has more reducing strength (*I*) (see Section VIII,A,3). This is connected to the greater π basicity of tungsten alkoxides, which is responsible for the enhanced metal-to-alkyne π^* backbonding that binds alkynes more tightly to tungsten (see above). The strong π -donor character of large alkoxide ligands increases the reducing power of the $(W\equiv W)^{6+}$ center to the point that complete reductive cleavage of the alkyne occurs. These electronic considerations contribute to the unique ability of $W_2(OR)_6$ compounds with bulky alkoxide ligands to promote cleavage of internal alkynes. The tendency of $Mo_2(OR)_6$ to catalyze alkyne cyclotrimerization and the lack of the same for $W_2(OR)_6$ also have an electronic origin. Cyclotrimerization requires reductive elimination of arene from intermediates derived from species like **12**. For the reasons outlined above, such a metal reduction step will be more facile for molybdenum than for tungsten (57).

4. Reactions with Nitriles

Ditungsten alkyne adducts undergo C—C bond-forming reactions with nitriles that give dimetallaheterobicyclic products (59,60). Thus, $W_2(\mu-C_2H_2)(O-t-Bu)_6(py)$ inserts 1 equiv $RC\equiv N$ ($R = Me, Ph$) to form $W_2[\mu-CHCHC(R)N](O-t-Bu)_6$, which has a structure based on **15**. Similarly,



$W_2(\mu-C_2Me_2)(OCH_2-t-Bu)_6(py)_2$ inserts 2 equiv $MeC\equiv N$ to form $W_2[\mu-N(CMe)_4N](OCH_2-t-Bu)_6(py)_2$, which has the heterocyclic ligand shown by **16**. A structure like **15** is a likely intermediate in the formation of **16**. These reactions have an obvious analogy to the alkyne oligomerization processes described above; **16** may resemble the intermediate in catalytic alkyne cyclotrimerization that yields arene by reductive elimination. An analogy to the ring-expansion chemistry of Section IV,B,3 is also apparent.

VI

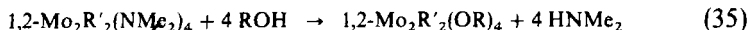
DINUCLEAR ALKYL AND ARYL COMPLEXES

A. Synthesis and Properties

1. Preparations

The Chisholm group has prepared a series of unbridged ethane-like dinuclear complexes fitting the general formula $M_2R'_x(OR)_{6-x}$. For convenience, the series is classified according to M and x.

a. $1,2-Mo_2R'_2(OR)_4$. Alcoholysis of molybdenum alkyl amide complexes proceeds according to Eq. (35) (61,62). The dimethyl compound



$R = t-Bu$; $R' = Me, CH_2-t-Bu, \text{ or } CH_2SiMe_3$

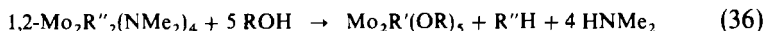
$R = i-Pr$; $R' = CH_2-t-Bu, CH_2SiMe_3, t-Bu, CH_2Ph, \text{ or } CH_2-4-C_6H_4Me$

$R = CH_2-t-Bu$; $R' = CH_2-t-Bu \text{ or } CH_2SiMe_3$

$R = Et$; $R' = CH_2-t-Bu \text{ or } CH_2SiMe_3$

forms a bis-pyridine adduct $1,2-Mo_2Me_2(O-t-Bu)_4(py)_2$. Only one example of a β -hydrogen-containing alkyl complex follows Eq. (35), $1,2-Mo_2(t-Bu)_2(O-i-Pr)_4$.

b. $1,2-Mo_2R'(OR)_5$. In general, the alcoholysis reactions for β -hydrogen-containing molybdenum alkyl complexes result in the loss of one alkyl ligand,



$R = t-Bu$; $R'' = R' = Et$

$R = t-Bu$; $R'' = n-Pr \text{ or } i-Pr$; $R' = 95\% i-Pr, 5\% n-Pr$

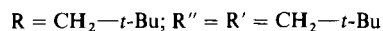
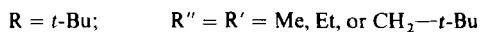
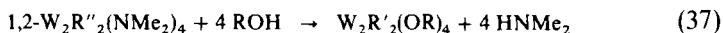
$R = t-Bu$; $R'' = i-Bu$; $R' = t-Bu$

$R = i-Pr$; $R'' = R' = Et$

$R = i-Pr$; $R'' = n-Pr$; $R' = 70\% i-Pr, 30\% n-Pr$

as shown in Eq. (36) (61–63). In several cases, rearrangement of the alkyl ligand also occurs. Mechanisms for these processes are discussed below.

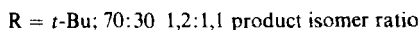
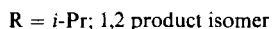
c. $1,2\text{-W}_2\text{R}'_2(\text{OR})_4$. Analogous tungsten compounds are prepared according to Eq. (37) (64). Three Eq. (37) products are isolated as Lewis base



adducts: $1,2\text{-W}_2\text{Me}_2(\text{O}-t\text{-Bu})_4(\text{py})_2$, $1,2\text{-W}_2\text{Ph}_2(\text{O}-i\text{-Pr})_4(\text{HNMe}_2)$, and $1,2\text{-W}_2(4\text{-C}_6\text{H}_4\text{Me})_2(\text{O}-i\text{-Pr})_4(\text{HNMe}_2)$. The latter two are rare examples of mono Lewis base adducts of the $(\text{M}\equiv\text{M})^{6+}$ center ($\text{M} = \text{Mo}$ or W); generally Lewis bases are bound cooperatively to give bis-ligand adducts (1). Alcoholysis of the tungsten amide complexes [Eq. (37)] is much faster than of the corresponding molybdenum amide complexes [Eq. (35)]. In contrast to molybdenum, several tungsten complexes with β -hydrogen-containing alkyl ligands are observed or isolated in Eq. (37); these will react further to generate $\text{W}_2\text{R}'(\text{OR})_5$ complexes [cf. Eq. (36)], but not cleanly. Alkyl isomerization is found in one case [Eq. (37), $\text{R}'' = i\text{-Pr}$].

d. $1,1,2\text{-W}_2\text{R}'_3(\text{OR})_3$. A single compound with this stoichiometry is known. Reaction of $1,1,2\text{-W}_2(\text{CH}_2-t\text{-Bu})_3(\text{NMe}_2)_3$ with $i\text{-PrOH}$ affords $1,1,2\text{-W}_2(\text{CH}_2-t\text{-Bu})_3(\text{O}-i\text{-Pr})_3$ (65).

e. $1,1\text{-}, 1,2\text{-Mo}_2\text{R}'_4(\text{OR})_2$. Metathetic exchange gives alkyl alkoxide complexes according to Eq. (38) (66,67). A mixture of isomers is obtained when



$\text{R} = t\text{-Bu}$ from which the 1,2 isomer is isolated. Formation of the 1,1 isomer in Eq. (38) indicates an alkyl migration has occurred. Alcoholysis of $1,1\text{-Mo}_2(\text{CH}_2\text{SiMe}_3)_4(\text{NMe}_2)_2$ affords $1,1\text{-Mo}_2(\text{CH}_2\text{SiMe}_3)_4(\text{O}-t\text{-Bu})_2$ on a preparative scale. Isolated 1,1- and $1,2\text{-Mo}_2(\text{CH}_2\text{SiMe}_3)_4(\text{O}-t\text{-Bu})_2$ do not interconvert at temperatures up to 100°C . The migration observed in Eq. (38) is thought to be base promoted (by LiOR) (67).

f. $\text{M}_2\text{R}'_5(\text{OR})$. Examples are known for the entire series of $\text{M}_2\text{R}'_x(\text{OR})_{6-x}$ compounds, from $\text{M}_2(\text{OR})_6$ to $\text{M}_2\text{R}'_6$ ($x = 0-6$), with a single exception: $\text{M}_2\text{R}'_5(\text{OR})$. We predict the latter should exist, and it might

be prepared from $\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_4(\text{O}-t\text{-Bu})\text{Br}$ (67) and an appropriate lithium alkyl.

2. Mechanism of Alcoholysis

On thermodynamic grounds, alcoholysis of $\text{M}-\text{R}'$ or $\text{M}-\text{NMe}_2$ bonds to give $\text{M}-\text{OR}$ bonds and alkane or HNMe_2 , respectively, are favorable reactions. Of the two, alcoholysis of $\text{M}-\text{R}'$ bonds should be most exothermic (62). We conclude that a *kinetic* preference for the alcoholysis of the $\text{M}-\text{NMe}_2$ unit exists [see Eqs. (35) and (37)], and it likely reflects the ease of protonation of an incipient nitrogen lone pair versus a metal-carbon σ bond.

The formation of $\text{Mo}_2\text{R}'(\text{OR})_5$ complexes according to Eq. (36) *only* when the alkyl ligands contain β -hydrogen atoms implies that β -H elimination is involved. Mechanistic studies suggest the following pathway (62). A β -hydrogen-containing $\text{Mo}_2\text{R}''_2(\text{NMe}_2)_4$ compound reacts with 4 equiv of ROH to give $\text{Mo}_2\text{R}''_2(\text{OR})_4$, as in Eq. (35). Subsequently, $\text{Mo}_2\text{R}''_2(\text{OR})_4$ undergoes β -H elimination and reductive elimination to liberate alkene and alkane (presumably via metal hydride intermediates). Alkene and alkane are spectroscopically detected. The elimination process generates a reduced metal species $\text{Mo}_2(\text{OR})_4$, which under certain conditions can be isolated as $\text{Mo}_2(\text{OR})_4(\text{L})_4$ ($\text{L} = \text{ROH}$ or HNMe_2). Then, in a metal reoxidation step, the $\text{Mo}_2(\text{OR})_4$ intermediate reacts with a fifth equivalent of ROH and the liberated alkene to form the final product, $\text{Mo}_2\text{R}'(\text{OR})_5$, such that the alcoholic proton is incorporated into the alkyl ligand.

This mechanism accounts for several important observations (62). When the alcoholysis is performed with deuterated alcohol, ROD, deuterium is incorporated into the β position of the alkyl ligand in the product. Reaction of $\text{Mo}_2(n\text{-Pr})_2(\text{NMe}_2)_4$ and $t\text{-BuOH}$ in the presence of 10 equiv of $\text{H}_2\text{C}=\text{CH}_2$ gives $\text{Mo}_2\text{Et}(\text{O}-t\text{-Bu})_5$, consistent with the proposed alkene loss from, followed by alkene readdition to, the dimetal center. Isomerization of alkyl ligands as noted above [see Eq. (36)] would result from H addition to the opposite end of the alkene from which initial β -H elimination occurred.

Alcoholysis reactions of $\text{Mo}_2\text{R}''_2(\text{NMe}_2)_4$ versus $\text{W}_2\text{R}''_2(\text{NMe}_2)_4$ differ in two significant ways: (1) the reactions are much faster for tungsten and (2) $\text{W}_2\text{R}'(\text{OR})_5$ complexes are not readily generated from β -hydrogen-containing alkyls. Tungsten is more electrophilic than molybdenum (see Section III,B,1,b) and will have a greater tendency to coordinate ROH. This might facilitate alcoholysis and would account for the faster rates. Tungsten is also more difficult to reduce than molybdenum (see Sections V,B,3 and VIII,A,3), so that the reductive elimination of alkane necessary in the formation of $\text{W}_2\text{R}'(\text{OR})_5$ complexes would be less favorable. Consequently, $\text{W}_2\text{R}'_2(\text{OR})_4$ complexes with β -hydrogen-containing alkyls are isolated more readily than their molybdenum counterparts. On further reaction with ROH, protonolysis of

tungsten-carbon bonds to give $W_2(OR)_6$ competes with the reductive elimination process, precluding isolation of $W_2R'(OR)_5$ products. By itself, β -H elimination does not change the oxidation state of the metal, and labeling studies and alkyl-ligand isomerization [see Eq. (37)] reveal that reversible β -H elimination occurs in the tungsten compounds. However, the reductive elimination of alkane that follows β -H elimination with the molybdenum alkyls is more difficult for tungsten.

3. Structure and Dynamics

The structure of $1,2-Mo_2Me_2(O-t-Bu)_4(py)_2$ is shown in Fig. 3 as a representative example (61). The $Mo\equiv Mo$ [2.256(1) Å] and $Mo-C$ [2.167(7) Å] distances are as expected for a $Mo_2 d^3-d^3$ dimer (1). In accord with our empirical rule for Lewis base coordination (see Sections IV,A,4 and V,A,2), pyridine is trans to carbon. One Mo d orbital at each Mo that would have participated in π bonding with alkoxide ligands is used in the $Mo-N$ σ bond. Hence, only a single Mo d orbital remains available for alkoxide π bonding, which can accept one electron pair, at each Mo. However, the coplanar $C-O-Mo-O-C$ segments pertaining to the mutually trans alkoxide ligands, evident in Fig. 3, indicate that *both* alkoxide ligands are π bonding with the *same* Mo d orbital. Thus, the two-electron π bonds are clearly delocalized over the approximately linear $O-Mo-O$ units to give delocalized $O p\pi-Mo d\pi-O p\pi$ bonding, with each alkoxide ligand donating half a lone pair. Such delocalization is more effective in the observed geometry having mutually trans alkoxides than in a hypothetical geometry having cis

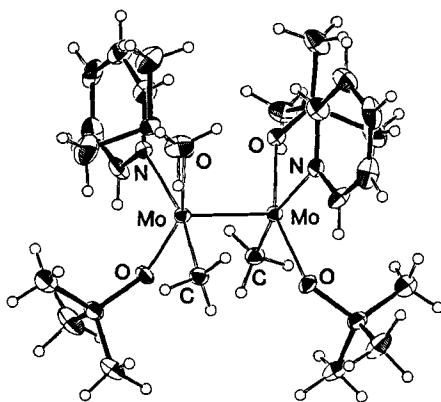


FIG. 3. ORTEP view of $1,2-Mo_2Me_2(O-t-Bu)_4(py)_2$ (61). Important bond distances (Å): $Mo-Mo = 2.256(1)$, $Mo-O = 1.92(6)$ (averaged), $Mo-C = 2.167(7)$, and $Mo-N = 2.349(6)$. Reprinted with permission from M. H. Chisholm, J. C. Huffman, and R. J. Tatz, *J. Am. Chem. Soc.* **105**, 2075. Copyright (1983) American Chemical Society (61).

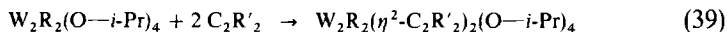
alkoxides and O—Mo—O angles of about 90°. The latter geometry would result from pyridine coordination cis to carbon rather than trans to carbon, as predicted by the empirical rule.

Because of the cylindrical symmetry of the d^3-d^3 $M\equiv M$ bond ($M = Mo, W$) a low barrier to rotation is expected (67), and anti and gauche isomers of $M_2R'_2(OR)_4$ rapidly equilibrate at room temperature (62,64). On cooling, this exchange becomes slow on the NMR time scale, and the barrier to anti-gauche interconversion measured for $Mo_2(CH_2-t-Bu)_2(OCH_2-t-Bu)_4$ is approximately 12 kcal/mol. Thermodynamic gauche:anti ratios for $M_2R'_2(OR)_4$ complexes are about 2–5:1. Dynamic behavior consistent with R' or OR migration across the $M\equiv M$ unit has *not* been observed by NMR for any $M_2R'_x(OR)_{6-x}$ compound.

B. Reactivity

1. Reactions with Alkynes

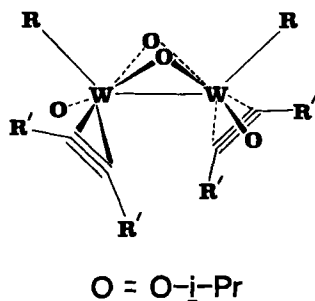
a. Bis- η^2 -Alkyne Adducts. As shown in Eq. (39), terminal alkyne complexes are obtained from reactions of $W_2R_2(O-i-Pr)_4$ complexes and



$R = Me, CH_2Ph, \text{ or } CH_2SiMe_3; R' = Me \text{ or } Et$

$R = n-Pr, C_6H_5, \text{ or } 4-C_6H_4Me; R' = Me$

alkynes (68,69). The structure of the bis- η^2 -alkyne adducts (17) consists of basal-edge-sharing square pyramids with two μ -OR ligands and an $M-M$

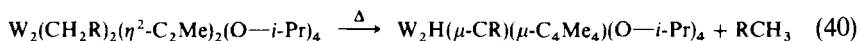


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single bond. Therefore, alkyne coordination is oxidative, converting a d^3-d^3 dimer to a d^1-d^1 dimer.

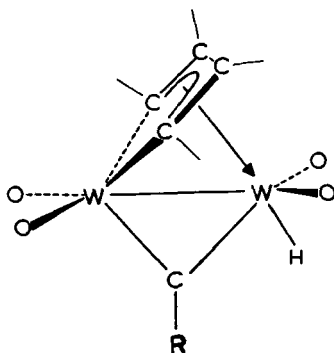
b. Conversion to Alkylidyne Hydride Complexes. When the alkyl ligands in $W_2R_2(\eta^2-C_2Me_2)_2(O-i-Pr)_4$ have α -hydrogen atoms, thermal decom-

position affords alkylidyne hydride complexes according to Eq. (40) (68,69). Several steps are implicated, including alkyne coupling to give the flyover ring



R = *t*-Bu, SiMe₃, and Ph

(see Section V,B,1), α -H transfer from one alkyl to the other to eliminate RCH₃, and α -H oxidative addition. No intermediates are detectable. When R is *t*-Bu, the products of Eq. (40) are obtained rapidly (-80°C) from reaction of W₂(CH₂-*t*-Bu)₂(O-*i*-Pr)₄ and 2 C₂Me₂, presumably via W₂(CH₂-*t*-Bu)₂(η^2 -C₂Me₂)₂(O-*i*-Pr)₄ [see Eq. (39)]. The structure of the alkylidyne hydride complexes is shown by **18**. Unusual chemical shifts of 19–21 ppm are



O = O-*i*-Pr

18

observed for the terminal hydride ligand by ¹H NMR. The origin of the unusual shifts is not understood but, speculatively, might in part reflect the diamagnetic anisotropy associated with the π -donor alkoxide ligands close to the hydride, for which the M—O bond order is clearly greater than 1.

The mechanism of Eq. (40) is under study (69). The reaction is first order in bis- η^2 -alkyne complex, and rates decrease in the order R = *t*-Bu > SiMe₃ > Ph. Activation parameters for R = SiMe₃, are $\Delta H^\ddagger_{\text{obs}} = +21(1)$ kcal/mol and $\Delta S^\ddagger_{\text{obs}} = -9(2)$ eu. Crossover experiments show that the process is unimolecular, and nondissociative in alkyne. A k_H/k_D value of 1.4 (60°C) is found for W₂(CH₂C₆H₅)₂(η^2 -C₂Me₂)₂(O-*i*-Pr)₄ versus W₂(CD₂C₆D₅)₂(η^2 -C₂Me₂)₂(O-*i*-Pr)₄. These results suggest that C—H bond breaking, bond forming, or alkane elimination are *not* occurring in the rate-determining step. We presently favor the proposal that a step *associated* with alkyne coupling is rate determining.

c. Alkyne Cleavage. Alkyne cleavage reactions promoted by $W_2(OR)_6$ were discussed in Section III,A,5. In a similar fashion, $W_2(CH_2-t-Bu)_2(O-i-Pr)_4$ and C_2Et_2 react to give $[W(\equiv CEt)(CH_2-t-Bu)(O-i-Pr)_2]_2$, which has a structure analogous to that in Fig. 2 (69). The chemistry of Eq. (39) is not observed.

d. $\mu-C_2R_2$ Adducts. Reactions of $1,2-W_2Me_2(O-t-Bu)_4(py)_2$ with alkynes do not lead to bis- η^2 -alkyne adducts or alkylidyne complexes as in paragraphs a–c above, but give thermally unstable $W_2(\mu-C_2R_2)$ complexes (69). In the case of C_2Me_2 , alkyl alkoxide migration accompanies $\mu-C_2Me_2$ adduct formation, and $1,1-W_2Me_2(\mu-C_2Me_2)(O-t-Bu)_4(py)$ is isolated. The structure, as shown in Fig. 4, is analogous to previously discussed $W_2(\mu-C_2R_2)$ adducts of type 10 (see Section V,A,2). From the reaction between C_2H_2 and $1,2-W_2Me_2(O-t-Bu)_4(py)_2$ a monomethyl complex $W_2Me(\mu-C_2H_2)(O-t-Bu)_5(py)$ has been isolated having a similar structure to that in Fig. 4; the mechanism of its formation is not clear.

Why does the chemistry of $1,2-W_2Me_2(O-t-Bu)_4(py)_2$ differ from that found for $1,2-W_2R_2(O-i-Pr)_4$ in Eq. (39)? The two obvious variations are the alkoxide ligands, $O-t-Bu$ versus $O-i-Pr$, and the presence of pyridine in the former case. Our examination of $M_2(\mu-C_2R_2)$ adducts in Section V,A,2

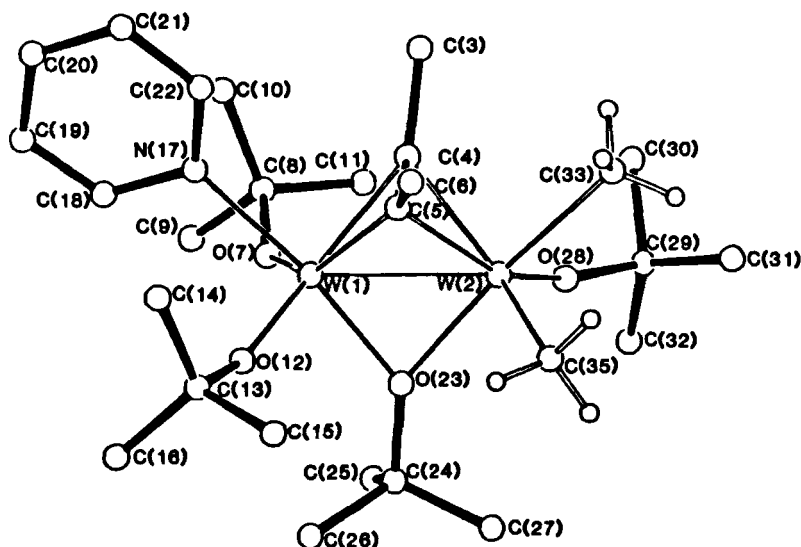


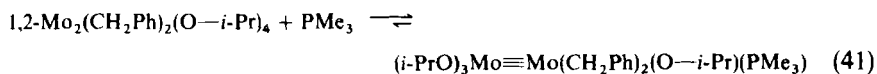
FIG. 4. Ball-and-stick view of $1,1-W_2Me_2(\mu-C_2Me_2)(O-t-Bu)_4(py)$. Important bond distances (Å, averaged where appropriate): $W-1-W-2 = 2.622(1)$, $C-4-C-5 = 1.412(19)$, $W-2-C-33 = 2.233(16)$, $W-2-C-35 = 2.162(16)$, $W-O-23 = 2.05(3)$, $W-2-O-28 = 1.873(11)$, $W-1-O-terminal = 1.91(3)$, and $W-1-N-17 = 2.216(12)$.

revealed that alkynes are most tightly bound when the complex is supported by the $\text{O}-t\text{-Bu}$ ligand versus smaller alkoxides. Second, Lewis bases can promote alkyl alkoxide migration (see below). Both considerations favor the observed $1,1\text{-W}_2\text{Me}_2(\mu\text{-C}_2\text{Me}_2)(\text{O}-t\text{-Bu})_4(\text{py})$ over the hypothetical $1,2\text{-W}_2\text{Me}_2(\eta^2\text{-C}_2\text{Me}_2)_2(\text{O}-t\text{-Bu})_4$ [refer to Eq. (39)].

e. Molybdenum Compounds. In contrast to the reactivity of $\text{W}_2\text{R}'_2(\text{OR})_4$ complexes with alkynes in paragraphs a–d above, the molybdenum analogs $\text{Mo}_2(\text{CH}_2-t\text{-Bu})_2(\text{O}-i\text{-Pr})_4$ and $\text{Mo}_2(\text{CH}_2\text{Ph})_2(\text{O}-i\text{-Pr})_4$ do not react with C_2H_2 or C_2Me_2 (69).

2. Reactions with Phosphines

Coordination of PMe_3 to $\text{Mo}_2(\text{CH}_2\text{Ph})_2(\text{O}-i\text{-Pr})_4$ results in alkyl alkoxide migration as shown in Eq. (41) (70). Available evidence suggests that



PMe_3 association precedes the migration process. An equilibrium exists between starting materials and product in Eq. (41) that is driven to the left on heating.

The related tungsten chemistry is more complicated (71). Addition of PMe_3 to $1,2\text{-W}_2(\text{CH}_2\text{Ph})_2(\text{O}-i\text{-Pr})_4$ gives the bis- PMe_3 adduct $1,2\text{-W}_2(\text{CH}_2\text{Ph})_2(\text{O}-i\text{-Pr})_4(\text{PMe}_3)_2$, which is stable only to 10°C . Under carefully controlled conditions, conversion to $(\text{i-PrO})_3\text{W}\equiv\text{W}(\text{CH}_2\text{Ph})_2(\text{O}-i\text{-Pr})(\text{PMe}_3)$ can be monitored. This alkyl alkoxide migration product is unstable, and it eliminates $\text{C}_6\text{H}_5\text{CH}_3$ and reacts further with PMe_3 to ultimately yield $(\text{i-PrO})_3\text{W}=\text{W}(\mu\text{-H})(\mu\text{-CPh})(\text{O}-i\text{-Pr})(\text{PMe}_3)_3$. The overall process converts a $(\text{W}\equiv\text{W})^{6+}$ center to a $(\text{W}=\text{W})^{8+}$ center, and is thus oxidative. Similar chemistry is observed for $1,2\text{-W}_2(\text{CH}_2\text{Ph})_2(\text{O}-i\text{-Pr})_4$ and PEt_3 , PMe_2Ph , or quinuclidene that ultimately gives $(\text{L})(\text{i-PrO})_2\text{W}=\text{W}(\mu\text{-H})(\mu\text{-CPh})(\text{O}-i\text{-Pr})_2(\text{L})$ ($\text{L} = \text{PEt}_3$, PMe_2Ph , or quin). These elimination processes are clearly relevant to Eq. (40).

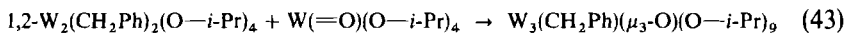
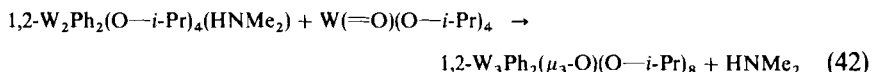
Two important observations come from the results above: (1) alkyl alkoxide migration is promoted by Lewis bases, and (2) alkyl alkoxide migration is a possible prerequisite to the toluene elimination process. Both observations have interesting implications for the alkane elimination reactions of Eqs. (36) and (40). Schrock has found that Lewis bases promote $\alpha\text{-H}$ elimination reactions from mononuclear bis-alkyl complexes, and has proposed that such promotion results from increased steric crowding around the metal center (7,12). Significantly, the net oxidative processes described in this section that lead to alkylidyne hydride complexes of ditungsten can be promoted by

either alkynes or phosphines, but in neither case are found for related dimolybdenum compounds. This is consistent with the greater resistance of molybdenum to oxidation (see Sections V,B,3, VIII,A,2, and VIII,A,3).

We have examined alkyl and aryl alkoxide complexes of varying stoichiometries, and their addition, migration, and elimination reactions with alcohols, alkynes, and phosphines. It is now instructive to consider what effect alkoxides have on alkyl complexes. Schrock finds that, relative to halide ligands, alkoxides stabilize alkyl complexes with respect to elimination reactions (12). He suggests that stability is decreased by an electrophilic metal center, and that alkoxides reduce metal electrophilicity (7). In our terminology, strong π -donor alkoxide ligands tie up metal orbitals that would otherwise be involved in β -H elimination and reductive elimination processes.

3. Cluster Formation

Comproportionation reactions similar to those discussed in Section III,B,3 proceed according to Eqs. (42) and (43) (69). Equation (43) is more complex



than a straightforward comproportionation; the reaction is under study. The structure of $1,2\text{-W}_3\text{Ph}_2(\mu_3\text{-O})(\text{O}-i\text{-Pr})_8$ is shown in Fig. 5. The new com-

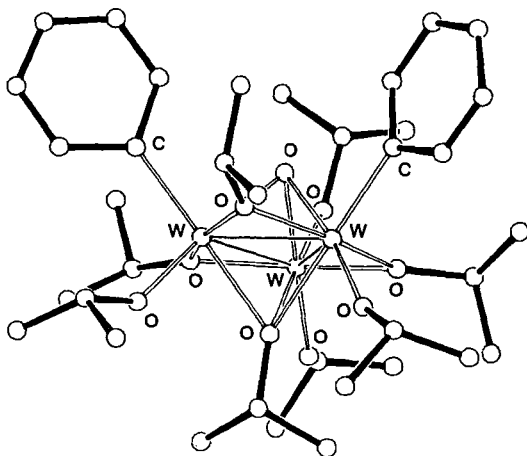


FIG. 5. Ball-and-stick view of $1,2\text{-W}_3\text{Ph}_2(\mu_3\text{-O})(\text{O}-i\text{-Pr})_8$. Important distances (\AA , averaged): $\text{W}-\text{W} = 2.55(1)$, $\text{W}-\text{C} = 2.11(4)$, and $\text{W}-\text{O}(\mu_3\text{-O}) = 2.07(3)$.

pounds are among the first examples of aryl and alkyl *clusters* of tungsten or molybdenum (72).

VII

POLYNUCLEAR ALKYLIDYNE COMPLEXES

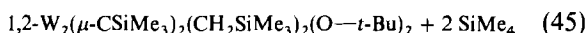
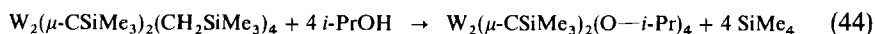
A. Synthesis and Properties

1. Preliminary Remarks

Section III described mononuclear alkylidyne complexes having terminal $M\equiv CR$ units. The alkylidyne fragment also functions as a bridging ligand, and $W_2(\mu-CR)$ complexes were products in reactions of dinuclear bis-alkyl complexes described in Section VI. A 1,3-dimetallacyclobutadiene intermediate was proposed in Section V that can be considered a bis- $(\mu-CR)$ compound. This section addresses the chemistry of bridging-alkylidyne complexes specifically, and is in large part a subset of more extensive studies of $W_2(\mu-CSiMe_3)_2(CH_2SiMe_3)_4$ chemistry reported by Chisholm and Heppert (73).

2. Preparation of Dinuclear Complexes

Alcoholysis reactions of $W_2(\mu-CSiMe_3)_2(CH_2SiMe_3)_4$ proceed according to Eqs. (44) and (45) (74,75). The product of Eq. (45) is formed as a mixture of



syn and anti isomers (structures discussed below), which do not react further with *t*-BuOH. A related complex was prepared by Cotton's group; the thermolysis of $W_2(O-t\text{-Bu})_6$ and C_2Ph_2 affords $W_2(\mu-CPh)_2(O-t\text{-Bu})_4$ in low yield, along with other products (55).

3. Structures

All of the $W_2(\mu-CR)_2X_4$ (X = alkyl or alkoxide) species discussed above are isostructural. A ball-and-stick view of $W_2(\mu-CSiMe_3)_2(O-i\text{-Pr})_4$ is shown in Fig. 6 (74). The W_2C_2 core is planar and has $W-C$ distances consistent with delocalized bonds of order 1.5. A second plane perpendicular

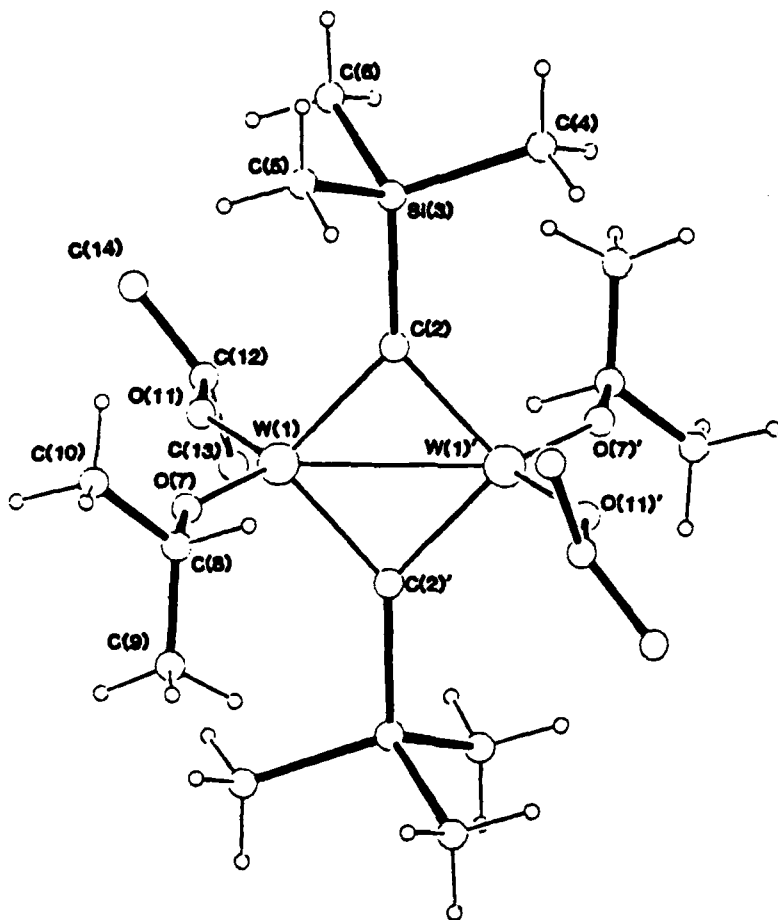
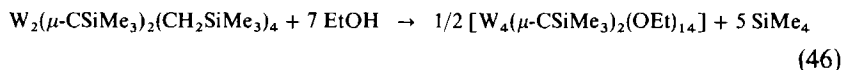


FIG. 6. Ball-and-stick view of $W_2(\mu\text{-CSiMe}_3)_2(\text{O-}i\text{-Pr})_4$ (74). Important distances (Å): $W\text{-}1\text{-}W\text{-}1' = 2.622(2)$, $W\text{-}1\text{-}O\text{-}7 = 1.86(1)$, $W\text{-}1\text{-}O\text{-}11 = 1.84(1)$, $W\text{-}1\text{-}C\text{-}2 = 1.97(2)$, and $Si\text{-}3\text{-}C\text{-}2 = 1.86(2)$. Reprinted with permission from M. H. Chisholm, J. C. Huffman, and J. A. Heppert, *J. Am. Chem. Soc.* **107**, 5116. Copyright (1985) American Chemical Society (74).

to the W_2C_2 plane contains both metal atoms and all four oxygen atoms. The $W\text{-}W$ distance of $2.622(2)$ Å reflects a single bond that is significantly lengthened by $O \rightarrow W$ π bonding (55,74). Complexes $W_2(\mu\text{-CSiMe}_3)_2(\text{O-}i\text{-Pr})_4$ and $W_2(\mu\text{-CPh})_2(\text{O-}t\text{-Bu})_4$ are the closest presently available analogs to the 1,3-dimetallacyclobutadiene intermediates **14** proposed in Section V,B,3.

4. Preparation of Polynuclear Complexes

The preparation of trinuclear alkylidyne complexes was discussed in Sections III,B,3 and V,B,2. Other syntheses of polynuclear alkylidyne complexes are described here. Ethanolysis of $W_2(\mu\text{-CSiMe}_3)_2(\text{CH}_2\text{SiMe}_3)_4$ proceeds according to Eq. (46) (37). The structure of the product contains a chain

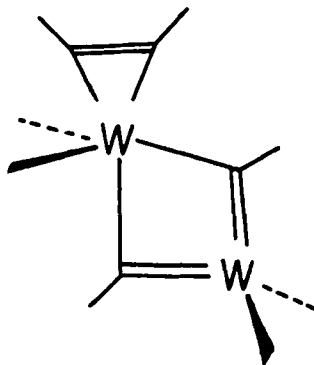


of four tungsten atoms with alternating short [2.516(1) Å] and long [3.513(1) Å] W—W distances, corresponding to single and non W—W bonding distances, respectively. Equations (44)–(46) demonstrate the existence of steric effects on the course of these alcoholysis reactions. Cotton and co-workers have reported that thermolysis of $W_2(\text{O}-t\text{-Bu})_6$ and 3-hexyne affords $[W_3(\text{O}-t\text{-Bu})_5(\mu\text{-O})(\mu\text{-CET})O]_2$ (76). The structure consists of two trinuclear W_3 units associated through two oxo bridges.

B. Reactivity

1. Reactions with Alkynes

To date, only dinuclear $\mu\text{-CR}$ complexes have been studied. Ethyne inserts into a $W_2(\mu\text{-CSiMe}_3)$ unit of $W_2(\mu\text{-CSiMe}_3)_2(\text{O}-i\text{-Pr})_4$ to give a 1,3-dimetalla allyl complex $W_2(\mu\text{-CHCHCSiMe}_3)(\mu\text{-CSiMe}_3)(\text{O}-i\text{-Pr})_4$ (74). The structure of the product is shown in Fig. 7. An intermediate is observed in the insertion reaction at low temperature. This intermediate, $W_2(\eta^2\text{-C}_2\text{H}_2)(\mu\text{-CSiMe}_3)_2(\text{O}-i\text{-Pr})_4$, has a terminal η^2 -alkyne ligand as shown by **19**.



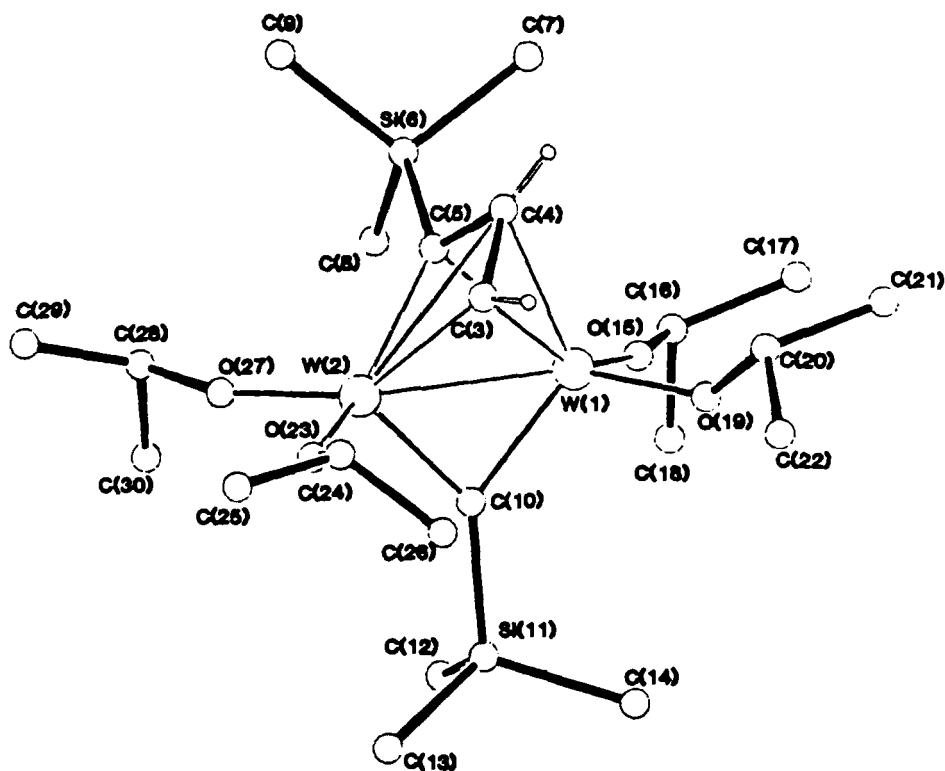


FIG. 7. Ball-and-stick view of $W_2(\mu\text{-CHCHCSiMe}_3)(\mu\text{-CSiMe}_3)(\text{O-}i\text{-Pr})_4$ (74). Important distances (Å, averaged where appropriate): $W\text{-}1\text{-}W\text{-}2 = 2.658(1)$, $W\text{-}O = 1.87(2)$, $W\text{-}1\text{-}C\text{-}3 = 2.33(1)$, $W\text{-}1\text{-}C\text{-}4 = 2.23(1)$, $W\text{-}1\text{-}C\text{-}5 = 2.14(1)$, $W\text{-}1\text{-}C\text{-}10 = 1.94(1)$, $W\text{-}2\text{-}C\text{-}3 = 2.10(1)$, $W\text{-}2\text{-}C\text{-}4 = 2.72(1)$, $W\text{-}2\text{-}C\text{-}5 = 2.15(1)$, and $W\text{-}2\text{-}C\text{-}10 = 1.96(1)$. Reprinted with permission from M. H. Chisholm, J. C. Huffman, and J. A. Heppert, *J. Am. Chem. Soc.* **107**, 5116. Copyright (1985) American Chemical Society (74).

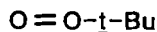
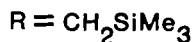
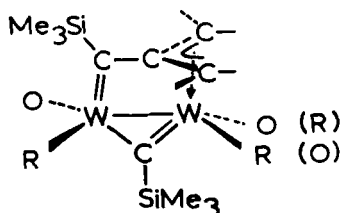
Similar chemistry is observed between the tetrakis-alkyl complex $W_2(\mu\text{-CSiMe}_3)_2(\text{CH}_2\text{SiMe}_3)_4$ and alkynes, with two important differences (74). The η^2 -alkyne intermediates $W_2(\eta^2\text{-C}_2\text{R}_2)(\mu\text{-CSiMe}_3)_2(\text{CH}_2\text{SiMe}_3)_4$ **19** are more stable than for the tetrakis-alkoxide complex above, and can in some cases be isolated and structurally characterized. Several ^{13}C -NMR parameters indicate that the alkyne is bound *less* tightly to $W_2(\mu\text{-CSiMe}_3)_2(\text{O-}i\text{-Pr})_4$ than to $W_2(\mu\text{-CSiMe}_3)_2(\text{CH}_2\text{SiMe}_3)_4$, including C_2R_2 chemical shifts and J_{WC} and J_{CC} coupling constants (74). This is easy to understand; alkyne and alkoxide ligands *both* have π -donor character and will compete for available W d π -acceptor orbitals. The second important difference is that the η^2 -alkyne adducts of the tetrakis-alkyl complex are also *kinetically* more inert, and insert

alkyne to form 1,3-dimetalla allyl complexes at slower rates. As discussed in Section III,B,1,b, tungsten-alkoxide bonds are polarized, $W^+—OR^-$, and this may induce polarization in the $W—C$ bond of the alkylidyne ligand. Such polarization for *terminal* $W\equiv CR'$ units was shown to enhance alkyne metathesis activity for $W(\equiv CR')(OR)_3$ complexes (see Section III,B,1). In the present case, such $W—C$ polarization may facilitate the insertion step that converts $W_2(\eta^2-C_2H_2)(\mu-CSiMe_3)_2(O-i-Pr)_4$ to $W_2(\mu-CHCHCSiMe_3)(\mu-CSiMe_3)(O-i-Pr)_4$.

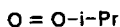
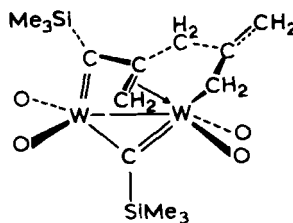
The $W_2(\mu-CHCHCSiMe_3)(\mu-CSiMe_3)X_4$ complexes ($X = CH_2SiMe_3$ or $O-i-Pr$) rearrange thermally to $W_2[\mu-CHC(SiMe_3)CH](\mu-CSiMe_3)X_4$, which places the bulky $SiMe_3$ substituent in the β position of the dimetalla allyl ligand (74). The rearrangement is faster for the tetrakis-alkyl complex. Activation parameters are as follows (77): $X = CH_2SiMe_3$, $\Delta H^\ddagger = +24.0(1.3)$ kcal/mol, $\Delta S^\ddagger = +9.3(4.6)$ eu; $X = O-i-Pr$, $\Delta H^\ddagger = +21.2(0.7)$ kcal/mol, $\Delta S^\ddagger = -16.3(2.0)$ eu. Thus, the differing rearrangement rates are traced to surprisingly and significantly different values for the entropic component of ΔG^\ddagger . Why is ΔS^\ddagger so negative for $X = O-i-Pr$ relative to $X = CH_2SiMe_3$? Speculatively, the reaction may require several $O \rightarrow W$ π bonds to be broken as the transition state is approached, either for conformational reasons, or to free up certain tungsten-centered orbitals for the rearrangement process.

2. Reactions with Allene

Allene and $W_2(\mu-CSiMe_3)_2(CH_2SiMe_3)_2(O-t-Bu)_2$ react to give a $W_2[\mu-CH_2(CH_2)CC(SiMe_3)]$ complex **20** (75). Similar insertion chemistry is found with 2 equiv of allene and $W_2(\mu-CSiMe_3)_2(O-i-Pr)_4$, leading to a product assigned structure **21** on the basis of spectroscopic data. In contrast to the



20

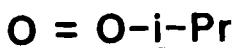
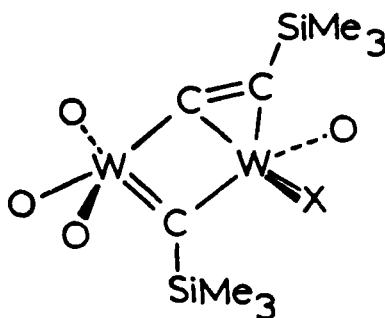
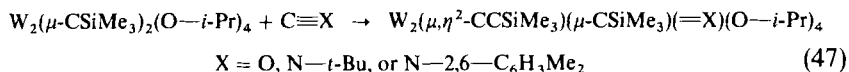


21

alkyne insertion reactions above, the rates of allene insertion decrease in the order $W_2(\mu\text{-CSiMe}_3)_2(\text{CH}_2\text{SiMe}_3)_4 > W_2(\mu\text{-CSiMe}_3)_2(\text{CH}_2\text{SiMe}_3)_2(\text{O}-t\text{-Bu})_2 > W_2(\mu\text{-CSiMe}_3)_2(\text{O}-i\text{-Pr})_4$.

3. Reactions with CO and Isonitriles

Isonitriles and CO undergo cleavage reactions according to Eq. (47) (78). The products adopt structure **22**. Such $\text{C}\equiv\text{O}$ cleavage is relevant to the



22

catalytic conversion of CO/H_2 to hydrocarbons, and will be discussed again in Section VIII,B,1.

VIII

CO, ISONITRILE, AND CARBIDE COMPLEXES

A. Synthesis and Properties

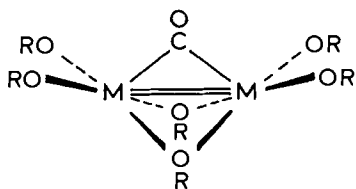
1. Preliminary Remarks

A large number of CO adducts of molybdenum and tungsten alkoxides have been prepared, and the area has been extensively summarized (79) and

reviewed (1,53). The present goal is to highlight a step-wise CO-reduction process that uses alkoxide complexes as reducing agents, to present theoretical results that pertain, and to outline some related isonitrile chemistry. In Section VIII,B (Reactivity), cleavage of CO to give carbide and oxide ligands is examined, and presently available examples of carbide alkoxide complexes are collected.

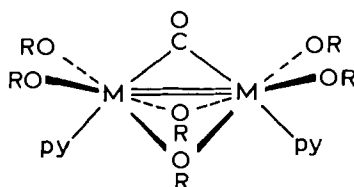
2. Preparation and Properties of Selected CO Adducts

Careful addition of CO to $M_2(OR)_6(py)_n$ compounds leads to adducts of type $M_2(\mu-CO)(OR)_6(py)_n$ **23** and **24** (53,79). Compounds **23** and **24** ($R = O-i-Pr$) have been structurally characterized and show $M-M$



$M = Mo \text{ or } W, R = t-Bu$

23



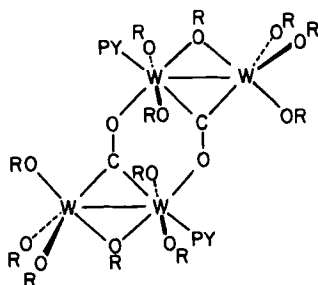
$M = Mo \text{ or } W, R = i-Pr \text{ or } CH_2-t-Bu$

24

and C—O distances consistent with double bonds for each (79–81). Note that pyridine coordinates trans to carbon in **24**, in accord with our empirical rule (see Sections IV,A,4 and V,A,2). Spectral data for **23** and **24** have been tabulated (53). The ν_{CO} values from IR spectra are in the range of $1567\text{--}1660\text{ cm}^{-1}$; these values are very low for $\mu\text{-CO}$ ligands and provide further evidence of substantial CO bond-order reduction in the alkoxide complexes.

The CO ligand is bound more tightly in the tungsten complexes than in the molybdenum complexes. This is reflected in the ease of CO dissociation and in structural and spectroscopic properties (53,79). CO is less dissociable, C—O and M—M bond distances are longer, and ν_{CO} values are lower in the tungsten compounds. We made the observation previously that tungsten alkoxides backbond to ligand acceptor orbitals more effectively than do molybdenum alkoxides (see Section V,A,2). The effect is present here as well, and a theoretical basis for it is developed below.

Dimerization of $W_2(\mu-CO)(O-i-Pr)_6(py)_2$ affords **25** (82). Structural (82) and spectroscopic (53) parameters indicate that further C—O and W—W bond-order reduction has occurred to give C—O and W—W single bonds. The base-free complex $[W_2(\mu,\eta^2-CO)(O-i-Pr)_6]_2$, which is closely related to **25**, has also been prepared (79).



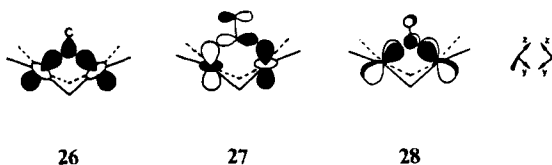
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The transformation of $W_2(O-i-Pr)_6(py)_2$ and $C\equiv O$ to $W_2(\mu-CO)(O-i-Pr)_6(py)_2$ and then to $1/2 [W_2(\mu,\eta^2-CO)(O-i-Pr)_6(py)]_2$ (**25**) corresponds to a step-wise reduction in CO bond order, from 3 to 2 to 1, as the CO bond distance goes from 1.13 to 1.22(4) to 1.33(3) Å, respectively. At the same time, the ditungsten center is converted from $(W\equiv W)^{6+}$ to $(W=W)^{8+}$ to $(W-W)^{10+}$, while W—C bonding increases, c.f. W—C = 2.06(3) Å in **24** versus 1.95(3) Å in **25**. Note well that tungsten is more effective than molybdenum at this ligand reduction process. Molybdenum will proceed only as far as $(Mo=Mo)^{8+}$ and a CO bond order of 2 in the compounds $Mo_2-(\mu-CO)(OR)_6(py)_n$.

3. Theoretical Studies of CO Adducts

The superior reducing power and π basicity of tungsten alkoxides relative to molybdenum alkoxides is a recurring theme in this article (see Sections III,B,1,b, V,A,2, V,B,3, VI,A,2, and VI,B,2). Additionally, the reduction of CO is a fundamental issue in organometallic chemistry. Hence, the CO adducts described above have been investigated by Fenske–Hall calculations to provide a theoretical complement to experimental results (83). Two questions are to be examined: (1) What orbital interactions are responsible for M—M and C—O bond-order reduction? and (2) Why are the tungsten compounds more effective at reduction and π backbonding than the molybdenum analogs?

This analysis takes a fragment MO approach, and considers interactions between $C_{2v} M_2(OH)_6$ and CO fragments. The binding of CO to the dimetal unit results from three important interactions, **26–28**. MO diagram **26** is the in-phase combination of the CO carbon-centered lone pair, n_σ , and a metal fragment acceptor orbital that is the in-phase combination of d_{z^2} atomic orbitals. MO diagram **27** is the in-phase combination between the CO π^* acceptor orbital parallel to the M—M axis, $\pi^*_{||}$, and a metal fragment donor



orbital that is the out-of-phase combination of d_{z^2} atomic orbitals. MO diagram **28** is the in-phase combination between the CO π^* -acceptor orbital perpendicular to the M—M axis, π^*_{\perp} , and a metal fragment donor orbital that is the in-phase combination of d_{xz} atomic orbitals.

The calculations suggest that metal-to-CO backbonding via **27** and **28** is the dominant mechanism for CO bond-order reduction, and that the $W_2(OH)_6$ fragment is more effective at such reduction than the $Mo_2(OH)_6$ fragment. Table II gives overlap populations for **27** and **28**. The populations, which are a measure of the strength of the $M_2(OH)_6$ and CO fragment orbital interactions, are larger for $W_2(OH)_6$ relative to $Mo_2(OH)_6$. The same trend is apparent in the CO fragment orbital populations of Table III. The population of the π^* orbitals of free CO is, of course, zero. On coordination of CO, the amount of electron density transferred to the CO π^* orbitals is a measure of

TABLE II
OVERLAP POPULATIONS BETWEEN $M_2(OH)_6$
AND CO FRAGMENT ORBITALS^a

Orbital	M = Mo	M = W
27	0.382	0.396
28	0.248	0.307

^a Adapted from Ref. 83.

TABLE III
MULLIKEN POPULATIONS OF CO FRAGMENT π^*
ORBITALS^a

Compound	π^*_{\perp}	π^*_{\parallel}
CO	0.000	0.000
$Mo_2(\mu-CO)(OH)_6$	0.428	0.732
$W_2(\mu-CO)(OH)_6$	0.530	0.835
$[W_2(\mu, \eta^2-CO)(OH)_6]_2$	0.914	1.174

^a Adapted from Ref. 83.

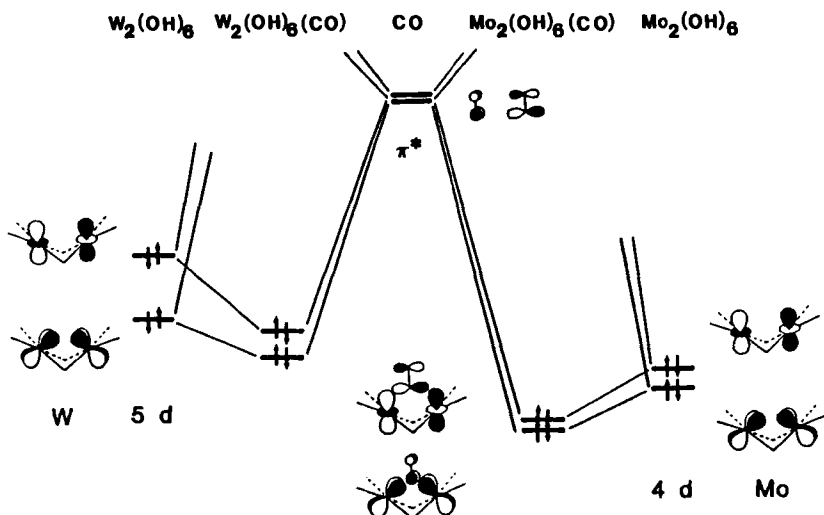


FIG. 8. Interaction diagram comparing carbonyl π^* -orbital interactions with molybdenum 4d and tungsten 5d $M_2(OH)_6$ fragment orbitals.

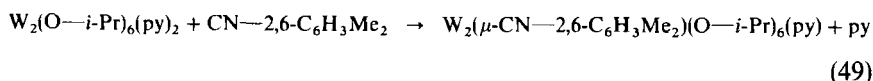
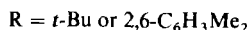
the extent of M-to-CO backbonding. Again, the populations are larger for $W_2(\mu-CO)(OH)_6$ relative to $Mo_2(\mu-CO)(OH)_6$.

Why does this happen? Refer to the interaction diagram in Fig. 8. Valence d orbitals for tungsten (5d) are higher lying than for molybdenum (4d), because the extra shell of core electrons shields tungsten valence electrons from nuclear charge to a greater degree. Consequently, tungsten valence orbitals are a better energy match for and interact more strongly with ligand acceptor orbitals (see Fig. 8).

Examination of the tetranuclear complex $[W_2(\mu,\eta^2-CO)(OH)_6]_2$ (see **25**) indicates that charge can be transferred to *both* ends of the CO π^* orbitals, since each end is now coordinated to a tungsten atom. Table III shows even higher populations in CO fragment orbitals, evidencing yet stronger W-to-CO backbonding. Additionally, the calculations show carbonyl O-to-W π donation via occupied CO π orbitals. As a result, CO is further reduced relative to $M_2(\mu-CO)(OH)_6$.

4. Isonitrile Adducts

Isonitriles react with tungsten alkoxides according to Eqs. (48) and (49) (84). The structure of $W_2(\mu-CN-2,6-C_6H_3Me_2)(O-t-Bu)_6$, shown in Fig. 9, is very similar to $M_2(\mu-CO)(OR)_6$ compounds (see above) and features a bent,



bridging CNR ligand. The C—N distance [1.274(27) Å] and C—N—C angle [130.1(19)°] are consistent with a C—NR double bond. The W—W distance [2.525(4) Å] also suggests a double bond. Thus, qualitatively identical bonding interactions are found in the $\text{W}_2(\mu\text{-CX})(\text{OR})_6$ compounds for X = O and NR. The IR $\nu_{\text{C}=\text{N}}$ values of 1525–1530 cm^{-1} are among the lowest ever observed for bridging isonitrile ligands. Therefore, $\text{W}_2(\mu\text{-CNR})$ complexes provide a predictable parallel to the CO chemistry discussed above.

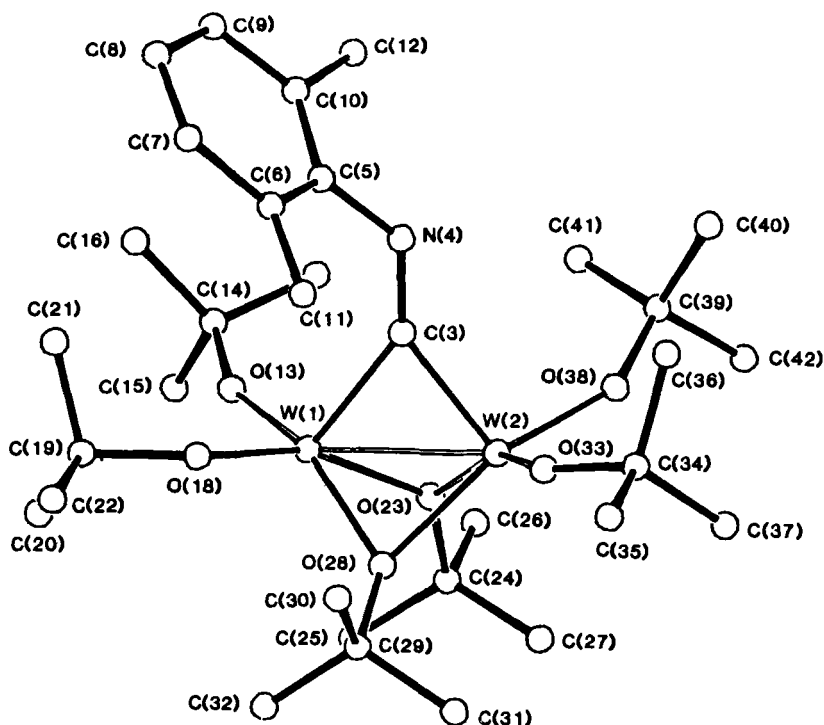


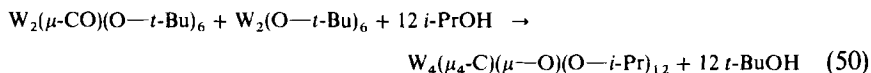
FIG. 9. Ball-and-stick view of $\text{W}_2(\mu\text{-CN}-2,6\text{-C}_6\text{H}_3\text{Me}_2)(\text{O}-t\text{-Bu})_6$. Important distances (Å, averaged where appropriate): W-1—W-2 = 2.525(4), W—O-bridging = 2.075(19), W—O-terminal = 1.884(26), W-1—C-3 = 2.098(21), W-2—C-3 = 1.988(23), and C-3—N-4 = 1.274(27).

B. Reactivity

1. CO Ligand Cleavage

The stepwise CO-reduction process above converts $\text{C}\equiv\text{O}$ and a $(\text{W}\equiv\text{W})^{6+}$ center ultimately to a $\mu,\eta^2\text{-(C-O)}$ ligand and a $(\text{W}-\text{W})^{10+}$ center. Further reduction would cleave the C—O bond entirely. A CO-cleavage reaction was described in Section VII,B,3 that gave a ditungsten oxo- σ , π -acetylide complex by formal insertion of the CO-derived carbon into a $\text{W}_2(\mu\text{-CSiMe}_3)$ unit [see Eq. (47)]. In the present case, C—O cleavage should afford a carbide oxide species. Experiments to test this possibility have been carried out by the Chisholm group.

A reaction of $\text{W}_2(\mu\text{-*CO})(\text{O}-t\text{-Bu})_6$ and reducing agent $\text{W}_2(\text{O}-t\text{-Bu})_6$ was carried out in the presence of excess *i*-PrOH (84). ^{13}C -NMR spectroscopy revealed the formation of a major resonance with four sets of tungsten satellites (see Fig. 10). The J_{WC} values of 180, 170, 40, and 30 Hz suggest two short (strong) and two long (weak) tungsten-carbon bonds, involving four inequivalent W atoms. The chemical shift, 347.75 ppm, is a reasonable value for a $(\mu\text{-C})^{4-}$ ligand (see below). On the basis of these data, formation of the $\text{W}_4(\mu_4\text{-C})$ cluster shown in Fig. 10, according to Eq. (50), is proposed.



However, a major side product is also obtained in this reaction, namely $[\text{W}_2(\mu,\eta^2\text{-CO})(\text{O}-i\text{-Pr})_6]_2$, and the proposed $\text{W}_4(\mu_4\text{-C})$ cluster has not yet been obtained in a pure state. Efforts to provide crystallographic verification of the proposed structure are in progress. Equation (50) models a reductive cleavage of $\text{C}\equiv\text{O}$ to C^{4-} and O^{2-} on a metal oxide. This is believed to be a fundamental step in Fischer-Tropsch chemistry, by which CO/H_2 is converted to hydrocarbon products.

2. Related Carbide Alkoxide Complexes

A persistent side product accompanies the preparation of $\text{W}_2(\text{O}-i\text{-Pr})_6(\text{HNMe}_2)_2$, in around 5–10% yields (85). Although difficult to obtain in preparative quantities, the compound has been characterized by elemental analysis, NMR spectroscopy, mass spectrometry, and X-ray crystallography as the carbido cluster $\text{W}_4(\mu_4\text{-C})(\mu\text{-NMe})(\text{O}-i\text{-Pr})_{12}$. A butterfly structure analogous to that in Fig. 10 is found, upon which that proposal (see above) is based. The ^{13}C -NMR resonance for the $(\mu_4\text{-C})^{4-}$ ligand is at 366.8 ppm.

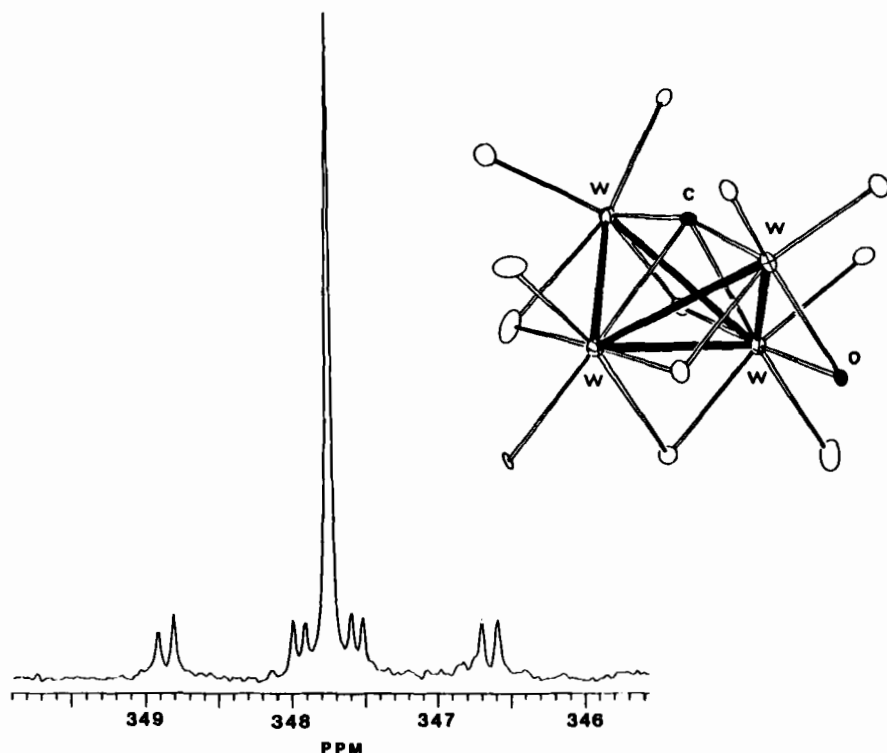
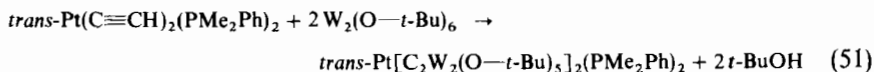


FIG. 10. The ^{13}C -NMR carbide resonances formed in the reaction of $\text{W}_2(\mu\text{-}^*\text{CO})(\text{O}-t\text{-Bu})_6$ with $\text{W}_2(\text{O}-t\text{-Bu})_6$ in the presence of $i\text{-PrOH}$, and the proposed structure of the carbide complex. With the exception of the darkened sphere representing the oxo group the other unmarked circles represent oxygen atoms of $\text{O}-i\text{-Pr}$ ligands taken from the structure of $\text{W}_4(\mu_4\text{-C})(\mu\text{-NMe})(\text{O}-i\text{-Pr})_{12}$.

A few examples of dicarbido (C_2) complexes are known. A platinum bis-acetylide complex reacts with $\text{W}_2(\text{O}-t\text{-Bu})_6$ according to Eq. (51) (86). The



pentanuclear product contains two $(\mu_3, \eta^2\text{-C}_2)^{4-}$ ligands. The C—C distance of 1.33(1) Å is consistent with a bond order of approximately 2. Schrock's group has prepared $(t\text{-BuO})_3\text{W}\equiv\text{C}-\text{C}\equiv\text{W}(\text{O}-t\text{-Bu})_3$ which contains the $(\mu\text{-C}_2)^{6-}$ unit (22). The latter compound has not been structurally characterized. Development of designed syntheses for carbide alkoxide complexes should be an interesting future research area.

IX

CONCLUSION

We have surveyed a broad range of organometallic chemistry of molybdenum and tungsten supported by alkoxide ligands. Three major themes were developed. (1) The strong π -donor character of alkoxide ligands controls the structures, stabilities, and reactivities of the compounds. Despite high formal oxidation states, alkoxide π donation provides electron-rich metal centers that interact strongly with carbon-based ligands having π^* -acceptor orbitals. (2) Compared to molybdenum alkoxides, tungsten alkoxides are more Lewis acidic as a result of greater M—OR bond polarity and generally greater M—L bond strengths. In the middle oxidation states, tungsten alkoxides are also more π basic and are stronger reducing agents than their molybdenum counterparts. (3) Examination of numerous structures suggests an empirical rule for Lewis base coordination to organometallic alkoxide complexes. Lewis bases coordinate in the geometry that *least* disrupts alkoxide-to-metal π donation, and this is *usually* trans to a carbon ligand.

This article is the only presently available *comprehensive* collection of the organometallic chemistry of molybdenum and tungsten alkoxides. We hope it will be a useful reference source for workers in the field and a useful introduction for those outside the field. The principles outlined herein can or have been applied to aryloxide complexes (87), other early transition metals, and lanthanide and actinide elements. Clearly, as spectator or ancillary ligands, alkoxides provide a new dimension to organometallic chemistry.

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A

- Acetylenes, reactions, with transition metal carbynes, 89–94
- Acid halides, reactions with anionic transition metal hydrides, 41–43
- Acids, reactions, with transition metal carbynes, 78–81
- Aggregation, in alkali metal organics, 178–181
 - ion size dependence, 179–181
 - solvation dependence, 179
- Alcoholysis, 346–347
- Aldehydes, reactions of
 - with anionic transition metal hydrides, 41–43
 - catalytic reduction, 44
 - with organoplatinum compounds, 118
- Alkali metals
 - ate complexes, *see* ate complexes, of mixed alkali metal compounds
 - halides, dimerization energies, 180
 - organometallic complexes, X-ray structural analysis, 169–277, *see also*, individual metals
 - aggregation, 178–181
 - alkyls, 191–192
 - alkynyls, 194–196
 - aryls and alkenyls, 192–194
 - benzyl compounds, 196–201
 - bond lengths, 185–190
 - bridging, 177–178
 - carbanion structures, without carbon-metal contacts, 238–260
 - with electron-withdrawing groups, 238–244
 - enolates, 254–260
 - radical anions, 245
 - transition metallates, 246–251
 - charge delocalization, 171–173
 - coordination, 176
 - cyclooctatetraene compounds, 203–205
 - cyclopentadienyl compounds, 201–203
 - graphite intercalates, 206–208
 - ion-dipole complexes, 236–238
 - ionicity, 174–176
 - ligand solvation, 181–185
 - mixed-metal compounds, 208–235
 - polyphenyl radical anions and poly-anions, 205–206
 - properties, 174
 - solvation energies, 182
- Alkenes
 - conversion to carbynes, 64–66
 - cycloaddition reaction, 300–306
 - metathesis reactions, 317–319
- Alkoxides, of molybdenum and tungsten carbide complexes, 364–365
 - carbonyl complexes
 - carbonyl cleavage reaction, 364
 - molecular orbitals, 361–362
 - synthesis, 359–360
 - theoretical studies, 360–362
- dinuclear alkyl and aryl complexes, 344–353
 - alcoholysis, 346–347
 - reactions, 348–353
 - with alkynes, 348–351
 - cluster formation, 352–353
 - with phosphines, 351–352
 - synthesis, 344–346
- dinuclear alkyne complexes, 337–344
 - reactions, 340–344
 - alkyne-bond formation, 340
 - alkyne cleavage, 342–343
 - with nitriles, 343–344
 - synthesis and structure, 337–339
- isonitrile adducts, 362–363
- metallacyclobutadiene complexes, 329–337
 - deprotio derivatives, 332–333
 - reactions
 - alkyne metathesis, 334–335
 - formation of cyclopentadienyl ligands, 335–336
 - ring expansion, 336–337
 - stability, 331–332
 - structures, 333–334
 - synthesis, 330–333
- mononuclear alkylidene complexes, 312–320
 - reactions
 - alkene metathesis, 317–319
 - coordination of Lewis bases, 319

- Alkoxides, of molybdenum and tungsten, mononuclear alkylidene complexes, reactions (*cont.*)
 rearrangement, 320
 Wittig reactions, 319–320
 spectroscopic data, 314
 structure, 315–316
 synthesis, 312–314, 316–317
mononuclear alkylidyne complexes, 320–329
 reactions
 alkyne metathesis, 325–327
 comproportionation reactions, 328
 coordination of Lewis bases, 327–328
 hydrolysis, 328–329
 structure, 323–325
 synthesis, 320–323
 by alkyne cleavage, 321–322
 by alkyne metathesis, 322–323
 from halides, 320–321
 by nitrile cleavage, 323
polynuclear alkylidyne complexes, 353–358
 reactions
 with alkynes, 355–357
 with allene, 357–358
 with carbon monoxide and isonitriles, 358
 structure, 353–354
 synthesis, 353, 355
Alkyl compounds, of alkali metals, 191–192, 218–219
Alkyl halides, reactions with anionic transition metal hydrides, 35–41
Alkylidenecyclopropanes, ring-opening reactions, 283–285
Alkynes, reactions of
 cleavage, in synthesis of tungsten alkoxides, 321–322
 metathesis
 in molybdenum and tungsten alkoxides, 325–327, 334–335
 in synthesis of tungsten alkoxides, 322–323
 of transition metal carbynes, 90
 with molybdenum and tungsten alkoxides, 348–351, 355–357
Alkynyl compounds, of alkali metals, 194–196, 219–220
Allene, reactions with tungsten alkoxides, 357–358
Allenyl complexes, of alkali metals, geometry, 178
Allyl silanes, elimination reactions, 285–287
Aluminum
 anionic hydride complexes, spectroscopic properties, 5
 mixed alkali metal compounds, 216–221, 223–236, 252
Americium, mixed alkali metal compounds, 256
Arsenic, anionic hydride complexes, spectroscopic properties, 5, 8
Aryl compounds, of alkali metals, 192–194, 219–220
ate complexes, of mixed alkali metal compounds, 218–235
 organoalkali compounds, 218–221
 alkyls, 218–219
 aryls and alkynyls, 219–220
 π delocalized anions, 220–221
nonorganic, 221–235
 halides, 228–231
 hydrides, 224–226
 oxides, 235
 pseudohalides, 231–232
 trimethylsilyl compounds, 221, 224
- B**
- Benzyl compounds, of alkali metals, 196–201
Beryllium, mixed alkali metal compounds, 226–227
Binuclear transition metal hydrides
 hydride ligand bonding, 16
 spectroscopic properties, 6–7, 23
 structural characteristics, 16–17
Biphenyl alkali metal radical anions, structural data, 245
Bonding, in transition metal carbynes, 52–53
Bond lengths, in alkali metal organics, 185–190
Bridging, in alkali metal organics, 177–178, 213
Brønsted acids, reactions with anionic transition metal hydrides, 33–34
- C**
- Cadmium, mixed alkali metal compounds, 220, 256
Calcium
 mixed alkali metal compounds, 221

- zeolites, 237
- Carbamoyl complexes, oxygen abstraction, 67-68
- Carbanions, alkali metal complexes, without carbon-metal interactions, 239-260
- Carbene complexes, of platinum(IV), 159-160
- Carbide complexes, *see* Alkoxides, of molybdenum and tungsten, carbide complexes
- Carbon monoxide, reaction with tungsten alkoxides, 358
- Carbonyl complexes
 - of alkali metal carbanions, 246-250
 - of anionic transition metal hydrides as catalysts, 44-46
 - interaction with sodium ions, 24
 - reactions, 28
 - with acid halides, aldehydes, and ketones, 41-43
 - with alkyl halides, 35-41
 - with Brønsted acids, 33-34
 - with Lewis acids, 30-33
 - spectroscopic properties, 4-7, 20-27
 - structural characteristics, 12-17
 - of molybdenum and tungsten alkoxides, *see* Alkoxides, of molybdenum and tungsten, carbonyl complexes
 - of platinum(IV), 158-159
 - of transition metal carbynes
 - bonding, 52-53
 - reactions, 70-79, 82-89, 94-103
 - structure, 53-55
 - synthesis, 57-60, 63-69
 - of trimethylenemethane metal complexes
 - reactions
 - with electrophiles, 294-295
 - with nucleophiles, 295-297
 - with tertiary phosphines, 297-298
 - synthesis, 280-289
 - structure, 290
- Carbyne complexes, of transition metals, *see* Transition metals, carbyne complexes
- Catalysts, 44-46
- Cesium
 - organometallic compounds, X-ray structural analysis, 169-277
 - aggregation, 180-181
 - alkyls, 191-192
 - bond lengths, 186, 190
 - bridging, 178
 - without carbon-metal interactions, 240-243, 245, 250-252, 254, 256
 - charge delocalization, 173
 - coordination, 176
 - graphite intercalates, 206-207
 - ionicity, 176
 - mixed metal compounds, 208-209, 212, 218-220, 226, 228-229, 231-232, 235
 - physical properties, 174
 - solvation energy, 182
- Chalcogen, reaction with organoplatinum halides, 128
- Chalcogenides, reactions, with transition metal carbynes, 94-95
- Charge delocalization, in alkali metal organics, 171-173
- Charge localization, in alkali metal enolates, 259
- Chelating agents, in alkali metal organics, 185
- Chloranil alkali metal compounds, structural data, 245
- Chromium
 - anionic hydride complexes
 - as catalyst, 45
 - reactions, 28-29
 - with acid halides, aldehydes, and ketones, 42-43
 - with alkyl halides, 35-38, 40-41
 - with Brønsted acids, 33
 - with Lewis acids, 30-32
 - spectroscopic properties, 4-7, 23-25
 - structure, 9-14
 - carbyne complexes
 - bonding, 52-53
 - reactions
 - carbyne cleavage, 97-98
 - carbyne coupling, 83-84
 - with nucleophiles, 70-75
 - spectroscopic properties, 56
 - structure, 53-55
 - synthesis, 57-59, 68
 - mixed alkali metal compounds, 214, 247, 249-250
 - trimethylenemethane complexes, synthesis, 281
- Cluster formation, by tungsten alkoxides, 352-353
- Cobalt
 - anionic hydride complexes
 - as catalysts, 44

- Cobalt, anionic hydride complexes (*cont.*)
 spectroscopic properties, 5, 23
 structure, 9–10
 carbyne complexes, reactions
 carbyne coupling, 84
 with nucleophiles, 74
 mixed alkali metal compounds, 209–211,
 217, 246–252, 256
 Comproportionation reactions, of
 molybdenum and tungsten alkoxides,
 328
 Coordination, in alkali metal organics, 176
 Coupling reactions, in transition metal car-
 bynes, 83–85
 Cyano derivatives, of anionic transition
 metal hydrides, as catalyst, 44
 Cycloalkane derivatives, of platinum,
 148–158
 Cyclooctatetraene compounds, of alkali
 metals, 203–205
 Cyclopentadienyl compounds, of alkali
 metals, 201–203, 243
 Cyclopentadienyl ligand formation, from
 tungstenacetylenediene alkoxide com-
 plexes, 335–336

D

- Dehalogenation, in synthesis of
 trimethylenemethane metal complexes,
 280–282
 β -Diketonate derivatives, of
 organoplatinum(IV), 145–148
 Dinuclear alkyl and aryl complexes, *see*
 Alkoxides, of molybdenum and
 tungsten, dinuclear alkyl and aryl com-
 plexes
 Dinuclear alkyne complexes, *see* Alkoxides,
 of molybdenum and tungsten,
 dinuclear alkyne complexes
 Disodium acetylide, crystal lattice, 196

E

- Electrophiles, reactions of
 with anionic transition metal hydrides,
 30–34
 with isonitrile and thiocarbonyl ligands,
 63–64
 with transition metal carbynes, 78–82
 with trimethylenemethane metal com-

- plexes, 294–295
 Elimination reactions, of allyl silanes,
 285–287
 Enolate derivatives, of alkali metal carban-
 ions, 254–258
 Ethylene, reactions with transition metal
 hydrides, 44
 Ethylsodium, crystal structure, 193
 Europium, mixed alkali metal compounds,
 215, 256

F

- Fluorenyllithium, bonding geometry, 177
 Fluorenylpotassium, bonding geometry, 177

G

- Gallium, anionic hydride complexes, spec-
 troscopic properties, 6
 Germanium
 anionic hydride complexes, spectroscopic
 properties, 4, 5
 mixed alkali metal complexes, 218, 224,
 232–233, 252
 Glycine, reaction with organoplatinum(IV)
 compounds, 119–120
 Gold
 anionic hydride complexes, structural
 characteristics, 16
 mixed alkali metal compounds, 250
 Graphite, intercalates of alkali metals,
 206–208

H

- Halides
 of mixed alkali metal compounds,
 228–231
 of triorganoplatinum(IV) compounds,
 126–127
 Halogenation, of platinum(II) complexes,
 114–115, 120–121
 Hydride ligand, bonding, in bimetallic com-
 plexes, 16
 Hydrides, of transition metals, *see* Transi-
 tion metals, hydrides
 Hydrolysis, of mononuclear alkylidyne
 complexes of tungsten alkoxides,
 328–329

I

- Indium, mixed alkali metal compounds, 218–221, 226
- Infrared spectroscopy
- of anionic transition metal hydrides, 20–22
 - of trimethylplatinum(IV) compounds, 132
- Ion–dipole complexes, of alkali metal organics, 236–238
- Ionicity, of alkali metal organics, 174–176
- Ion pairing
- in alkali metal organics, 184–185
 - in anionic transition metal hydrides, 24–27
- Iridium
- anionic hydride complexes, spectroscopic properties, 5
 - trimethylenemethane complexes
 - reactions
 - with nucleophiles, 296–297
 - with silver hexafluorophosphate, 299–300
 - with tertiary phosphines, 297–298
 - role in organic synthesis, 306
 - structure, 289–290
 - synthesis, 285–286
- Iron
- anionic hydride complexes
 - as catalyst, 44–45
 - reactions, 28–29
 - with acid halides, 41
 - with aldehydes, 43
 - with alkyl halides, 35–37, 40–41
 - with Brønsted acids, 33–34
 - with Lewis acids, 32–33
 - with small electrophiles, 34
 - spectroscopic properties, 4–5, 7, 20–21, 23–24, 26–27
 - structure, 9, 15–17
- carbyne complexes
- reactions
 - carbyne coupling, 85
 - with nucleophiles, 77
 - structure, 55
 - synthesis, 58
- mixed alkali metal compounds, 246–250, 256
- trimethylenemethane complexes
- orbital diagram, 291
 - reactions, 299
 - with electrophiles, 294–295

- redox reactions, 298
 - with tertiary phosphines, 297
 - role in organic synthesis, 301
 - structure and bonding, 289–292
 - synthesis, 280–284, 287–289
- Isonitrile complexes, *see* Alkoxides, of molybdenum and tungsten, isonitrile complexes
- Isonitriles, reactions of
- with electrophiles, 63–64
 - with tungsten alkoxides, 358

K

- Ketenyl compounds, formation, from transition metal carbynes, 75–77
- Ketones, reactions, with anionic transition metal hydrides, 41–43

L

- Lead, anionic hydride complexes, spectroscopic properties, 4
- Lewis acids
- reactions with anionic transition metal hydrides, 30–33
 - reactions, with transition metal carbynes, 81–82
 - in synthesis of transition metal carbynes, 56–59
- Lewis bases, coordination by molybdenum and tungsten alkoxides, 319, 327–328
- Ligand solvation, in alkali metal organics, 181–185
- anion solvation, 185
 - chelating agents, 185
 - heteroatom effects, 184
 - ion pairing and aggregation, 184–185
 - solvation energies, 182–184
- Lithium
- base affinities, 183
 - organometallic compounds, X-ray structural analysis, 169–277
 - aggregation, 178–181
 - alkynyls, 195–196
 - aryls and alkenyls, 192, 194
 - benzyl compounds, 196–198, 201
 - bond lengths, 186
 - bridging, 177–178
 - coordination, 176

Lithium, organometallic compounds, X-ray
structural analysis (*cont.*)
cyclopentadienyl derivatives, 201, 203
enolates, 252–253
graphite intercalates, 208
ionicity, 174–176
ligand solvation, 181–185
mixed metal compounds, 211–212,
214–217, 219, 226, 229
physical properties, 174
salts, of transition metal hydrides, 6–8,
19, 24–26
solvation energy, 182

M

Magnesium, mixed alkali metal compounds,
220

Manganese

anionic hydride complexes
reactions, with Lewis acids, 32–33
spectroscopic properties, 5, 23
structure, 9
carbyne complexes
bonding, 52–53
reactions
carbyne coupling, 84
with nucleophiles, 70–71, 74, 77
structure, 55
synthesis, 58, 66

Meisenheimer salts, of carbanions, 243

Mercury, mixed alkali metal compounds,
247, 252

Metallacyclobutadiene complexes, *see*
Alkoxides, of molybdenum and
tungsten, metallacyclobutadiene com-
plexes

Methyl anion, molecular orbitals, 172

Methylpotassium, crystal structure, 192

Methylsodium, crystal structure, 191

Mixed-metal compounds, of alkali metal
organics, 208–235

Molecular orbitals

of methyl anion, 172
of molybdenum and tungsten alkoxides,
316, 361–362
of trimethylenemethane metal complexes,
291, 293, 294

Molybdenum

alkoxides, 311–369
carbonyl complexes

molecular orbitals, 361–362

structure, 359–360

synthesis, 359–360

dinuclear alkyl and aryl complexes

reactions, 351

structure, 347–348

synthesis, 344–346

dinuclear alkyne complexes

reactions, 340, 343

synthesis and structure, 337–339

metallacyclobutadiene complexes,
332–333

ring expansion, 336–337

structure, 334

mononuclear alkylidyne complexes

reactions, 325–328

synthesis, 321–322

anionic hydride complexes

as catalyst, 45

reactions, 28–29

with Brønsted acids, 33–34

with ketones, 43

spectroscopic properties, 4–7, 23

structural characteristics, 12–16, 18–19

carbyne complexes

as catalyst in alkene metathesis, 90

reactions

with acetylenes, 93–94

with acids, 79–80

with carbon monoxide, 99

carbyne coupling, 84

with chalcogenides, 95

with Lewis acids, 82

with metal complexes, 88

with nucleophiles, 72–76

photolysis, 98

transformation to vinylidenes, 95–97

with xylylisocyanide, 99

spectroscopic properties, 56

structure, 54

synthesis, 57–58, 62–68

mixed alkali metal compounds, 251

trimethylenemethane complexes

reactions, with nucleophiles, 295–297

structure, 289, 292

synthesis, 284

Mononuclear alkylidene complexes, *see*

Alkoxides, of molybdenum and

tungsten, mononuclear alkylidene com-
plexes

Mononuclear alkylidyne complexes, *see*

- Alkoxides, of molybdenum and tungsten, mononuclear alkylidyne complexes
- Monosodium acetylide, crystal structure, 195
- N**
- Nickel
- anionic hydride complexes
 - reactions, with Lewis acids, 31
 - spectroscopic properties, 5–7
 - structural properties, 15–18
 - carbyne complexes, coupling reactions, 84
 - mixed alkali metal compounds, 211–215, 249, 252
 - trimethylenemethane complexes
 - in organic synthesis, 301, 306–307
 - synthesis, 285
- Niobium
- anionic hydride complexes, spectroscopic properties, 4, 6, 24–25
 - mixed alkali metal compounds, 212, 251
- Nitrile cleavage reactions, in synthesis of tungsten alkoxides, 323
- NMR, *see* Nuclear magnetic resonance spectroscopy
- Nuclear magnetic resonance spectroscopy
- of anionic transition metal hydrides, 22–24
 - of trimethylenemethane osmium complexes, 292
 - of trimethylplatinum(IV) compounds, 132
 - of tungsten alkoxides, 314
- Nucleophiles, reactions of
- with transition metal carbynes, 69–77
 - with trimethylenemethane metal complexes, 295–297
- O**
- Organoplatinum complexes, *see* Platinum, organic chemistry
- Osmium
- anionic hydride complexes
 - spectroscopic properties, 5, 8, 23
 - structural properties, 18
 - carbyne complexes
 - reactions
 - with acids, 78
 - carbyne coupling, 84–85
 - with chalcogenides, 94–95
 - with metal complexes, 85–86
 - photolysis, 98
 - transformation to vinylidenes, 96
 - structure, 55
 - synthesis, 69
 - trimethylenemethane complexes
 - nuclear magnetic resonance spectrum, 292
 - reactions, with electrophiles, 294–295
 - synthesis, 285
- Oxidative addition reactions, of organoplatinum complexes, 114, 116, 120–121, 124–125, 128–130, 159–160
- Oxides, of mixed alkali metal compounds, 235
- P**
- Palladium
- anionic hydride complexes, spectroscopic properties, 5
 - mixed alkali metal compounds, 256
 - trimethylenemethane complexes
 - role in organic synthesis, 301–307
 - synthesis, 285
- Phenyl bridge, in mixed metal organics, 212–215
- Phosphine derivatives, of anionic transition metal hydrides
- reactions, 32–34
 - with alkyl halides, 35, 37–41
 - with electrophiles, 33
 - spectroscopic properties, 5, 21, 23–27
 - structural characteristics, 9–10, 12–20
- Phosphines, reactions
- with molybdenum and tungsten alkoxides, 351–352
 - with trimethylenemethane metal complexes, 297–298
- Photochemical reactions, of transition metal carbynes, 98
- Photolysis, of platinacycloalkanes, 152
- Platinum
- anionic hydride complexes
 - as catalyst, 46
 - spectroscopic properties, 5
 - mixed alkali metal compounds, 251, 256
 - organic chemistry, of platinum(IV), 113–168
 - carbenes, 159
 - carbonyl complexes, 158–159
 - crystallographic data, 122–123
 - cycloalkane derivatives, 148–158

- Platinum, organic chemistry, of
 platinum(IV) (*cont.*)
 β -diketonates, 145–148
 diorganoplatinum(IV) compounds,
 117–126
 isocyanide derivatives, 160–161
 monoorganoplatinum(IV) compounds,
 114–117
 tetraorganoplatinum(IV) compounds,
 143–145
 triorganoplatinum(IV) compounds,
 126–143
 bond lengths and angles, 138
 chemical properties, 141–143
 group V and VI donor ligands,
 127–131
 halides and pseudohalides, 126–127
 spectroscopic properties, 131–143
 trimethylenemethane complexes
 role in organic synthesis, 305–307
 structure, 294
Polyhapto-coordinated mixed metal com-
 plexes, 208–212
Polymerization
 of alkali metal organics, 179–180
 of transition metal carbynes, 94
Polymers, of organoplatinum compounds,
 117–118
Polyphenyl alkali metal compounds, radical
 anions and dianions, 205–206
Potassium
 organometallic compounds, X-ray struc-
 tural analysis, 169–277
 aggregation, 179–181
 alkyls, 191–192
 alkynyls, 194–196
 benzyl compounds, 198–200
 biphenyl radical anion, 206
 bond lengths, 186, 188–189
 bridging, 177–178
 without carbon–metal interactions,
 239–243, 245, 248–259
 charge delocalization, 173
 coordination, 176
 cyclooctatetraene compounds, 204–205
 cyclopentadienyl derivatives, 203
 graphite intercalates, 206–207
 ionicity, 176
 mixed metal compounds, 208–211, 213,
 216, 218–235
 physical properties, 174
 salts, of anionic transition metal hydrides
 spectroscopic properties, 5–8, 21
 structural properties, 12–14, 18–19,
 24–25
 solvation energy, 182
 zeolites, 237–238
Praseodymium, mixed alkali metal com-
 pounds, 251
Pseudohalide derivatives, of mixed alkali
 metal compounds, 231–232
Pyrolysis
 of organoplatinum(IV) complexes, 126, 142
 of platinacycloalkanes, 152–154
- R**
- Rearrangement, of tungsten alkoxides, 320
Redox reactions, of trimethylenemethane
 metal complexes, 298
Reductive coupling reactions, of transition
 metal carbynes, 83
Reductive elimination, in
 organoplatinum(IV) complexes,
 125–126, 141–142
Reppé reaction, 44
Rhenium
 anionic hydride complexes
 spectroscopic properties, 4, 7, 8, 21–22,
 25
 structure, 9–11, 17
 carbyne complexes
 reactions, with nucleophiles, 70–71,
 74–75, 77
 structure, 55
 synthesis, 61–63, 69
 mixed alkali metal compounds, 250
Rhodium
 anionic hydride complexes, spectroscopic
 properties, 5
 mixed alkali metal compounds, 247–248,
 250
 trimethylenemethane complexes
 role in organic synthesis, 305–306
 synthesis, 285–286
Ring expansion, in molybdenacyclobutadiene
 alkoxide complexes, 336–337
Ring opening reactions, of
 alkylidenecyclopropanes, 283–285
Rubidium
 organometallic compounds, X-ray struc-
 tural analysis, 169–277

- aggregation, 180–181
 - alkyls, 191–192
 - alkynyls, 194
 - bond lengths, 186, 190
 - bridging, 177
 - without carbon–metal interaction, 239–242, 245, 250, 254, 255, 257–258
 - charge delocalization, 173
 - coordination, 176
 - cyclooctatetraene compounds, 204
 - graphite intercalates, 206–207
 - ionicity, 176
 - mixed metal compounds, 218–220, 231, 233
 - physical properties, 174
 - solvation energy, 182
 - Ruthenium
 - anionic hydride complexes
 - as catalyst, 45
 - reactions
 - with alkyl halides, 36–37
 - with Brønsted acids, 33
 - spectroscopic properties, 5, 8, 21, 23
 - structural properties, 18
 - carbyne complexes, coupling reactions, 85
 - mixed alkali metal compounds, 209–210, 251
 - trimethylenemethane complexes
 - role in organic synthesis, 306
 - synthesis, 285
- S**
- Salicylaldehyde, reaction with
 - organoplatinum compounds, 118
 - Selenium, mixed alkali metal compounds, 228–229
 - Sodium
 - organometallic compounds, X-ray structural analysis, 169–277
 - aggregation, 180
 - alkyls, 191–193
 - alkynyls, 194–196
 - aryls and alkenyls, 192–194
 - benzyl compounds, 196–199
 - bond lengths, 186–188
 - bridging, 178
 - without carbon–metal interactions, 245–247, 251–252, 254–256, 258
 - charge delocalization, 173
 - coordination, 176
 - cyclopentadienyl derivatives, 201–202
 - graphite intercalates, 208
 - ionicity, 176
 - mixed metal compounds, 211–221, 223–227, 246–247, 251–252
 - polyphenyl radical anions and dianions, 205–206
 - physical properties, 174
 - salts, of anionic hydride complexes
 - spectroscopic properties, 4–8, 24–27
 - structural properties, 18
 - solvation energy, 182
 - zeolites, 236–237
 - Sodium terphenyl, radical anion and dianion, 205
 - Solvation energies, in alkali organics, 182–184
 - Spectroscopic properties
 - of anionic transition metal hydrides, 4–8, 20–27
 - of organoplatinum(IV) complexes, 131–143
 - of transition metal carbynes, 55–56
 - of tungsten alkoxides, 314
 - Structure
 - of alkali–graphite intercalates, 207
 - of alkali metal carbanions with no carbon–metal interactions, 239–242
 - of anionic transition metal hydrides, 9–20
 - of benzylic alkali metal complexes, 197–200
 - of cyclooctatetraenepotassium compounds, 205
 - of cyclopentadienyl alkali metal complexes, 201–203
 - of ethylsodium, 193
 - of methylpotassium, 192
 - of methylsodium, 191
 - of mixed alkali metal compounds, 208–216, 218–235
 - of molybdenum and tungsten alkoxides
 - carbonyl complexes, 359–360
 - dinuclear alkyl and aryl complexes, 347–348
 - dinuclear alkyne complexes, 338–339
 - metallacyclobutadiene complexes, 333–334
 - mononuclear alkylidene complexes, 315–316
 - mononuclear alkylidyne complexes, 323–325

- Structure, of molybdenum and tungsten alkoxides (*cont.*)
 polynuclear alkylidyne complexes, 353–354
 of monosodium acetylide, 195
 of organoplatinum(IV) compounds, 121, 138–141, 144, 157
 of phenylsodium•pentamethyldiethylene-triamine, 193
 of potassium biphenyl radical anion, 206
 of sodium terphenyl radical dianion, 205
 of transition metal carbynes, 53–55
 of trimethylenemethane metal complexes, 289–294
- Substitution reactions, in transition metal carbynes, 95
- Synthesis
 of molybdenum and tungsten alkoxides carbonyl complexes, 359–360
 dinuclear alkyl and aryl complexes, 344–346
 dinuclear alkyne complexes, 337–339
 isonitrile complexes, 362–363
 metallacyclobutadiene complexes, 330–333
 mononuclear alkylidene complexes, 312–314, 316–317
 mononuclear alkylidyne complexes, 320–323
 polynuclear alkylidyne complexes, 353, 355
 of transition metal carbynes, 56–69
 of trimethylenemethane metal complexes, 279–289
- ## T
- Tantalum
 anionic hydride complexes, spectroscopic properties, 4
 carbyne complexes
 reactions, with acetylenes, 91
 structure, 54
 synthesis, 59–61
 trimethylenemethane complexes, synthesis, 283
- Technetium, anionic hydride complexes, spectroscopic properties, 8, 21
- Tetracyanochinodimethane alkali metal compounds, structural data, 245
- Thermal extrusion, in synthesis of trimethylenemethyl metal complexes, 282–283
- Thiocarbonyl ligands, reactions with electrophiles, 63–64
- Tin
 anionic hydride complexes, spectroscopic properties, 4, 5
 carbyne complexes, synthesis, 69
- Titanium, anionic hydride complexes, spectroscopic properties, 8
- Transition metals, *see also* specific metals
 carbyne complexes, 51–111
 bonding, 52–53
 as reaction intermediates, 100–101
 reactions, 69–103
 with acetylenes, 89–94
 acid-induced coupling, 83–84
 with acids, 78–81
 alkyne metathesis, 90
 with chalcogenides, 94–95
 cleavage of carbyne, 97–98
 coupling of carbyne ligands, 83–85
 with electrophiles, 78–82
 formation of ketylenyl compounds, 75–77
 with Lewis acids, 81–82
 with metal complexes, 85–89
 nucleophilic addition, 70–72
 nucleophilic substitution, 72–75
 photochemical reactions, 98
 polymerization, 94
 reductive coupling, 83
 substitution of carbyne, 95
 transformation to vinylidenes, 95–97
 structure, 53–55
 synthesis, 56–69
 hydrides, anionic, 1–50, *see also* specific compounds
 as catalysts, 44–46
 interaction with sodium ions, 24
 ion pairing, 23–27
 reactions, 28–43
 with acid halides, aldehydes, and ketones, 41–43
 with alkyl halides, 35–41
 with Brønsted acids, 33–34
 with electrophiles, 30–34
 with Lewis acids, 30–33
 scope, 28–30
 spectroscopic properties, 4–8, 20–27
 structural characteristics, 9–20
 mixed alkali metal compounds, 208–216, 246–251

- Trimethylenemethane, cycloaddition to alkenes, 300–304
- Trimethylenemethane metal complexes, 279–309
- reactions, 294–300
 - with electrophiles, 294–295
 - modification reactions, 299–300
 - with nucleophiles, 295–297
 - redox reactions, 298
 - with tertiary phosphines, 297–298
- role in organic synthesis, 300–307
- structure and bonding, 289–294
- synthesis, 279–289
- from allyl silanes, 285–287
 - by dehalogenation, 280–282
 - miscellaneous methods, 287–289
 - by ring opening of alkylidenecyclopropanes, 283–285
 - by thermal extrusion, 282–283
- Trimethylsilyl mixed alkali metal compounds, 221, 224
- Tris(carbonyl)- η^4 -trimethylenemethaneiron
- reactions
 - with electrophiles, 294
 - with tertiary phosphines, 297–298
 - role in organic synthesis, 301
 - structure, 289–290
- Tungsten
- alkoxides, 311–369
 - carbide complexes, 364
 - carbonyl complexes
 - carbonyl cleavage reaction, 364
 - molecular orbitals, 361–362
 - structure, 359–360
 - synthesis, 359–360
 - theoretical studies, 360–362
 - dinuclear alkyl and aryl complexes
 - reactions, 348–353
 - structure, 348
 - synthesis, 345
 - dinuclear alkyne complexes
 - reactions, 340–344
 - synthesis and structure, 337–339
 - isonitrile adducts, 362–363
 - metallacyclobutadiene complexes, 330–332
 - reactions, 333–336
 - stability, 331–332
 - structure, 333–334
 - synthesis, 330–331
 - mononuclear alkylidene complexes
 - reactions, 317–320
 - spectroscopic data, 314
 - synthesis, 312–314, 316–317
 - mononuclear alkylidyne complexes
 - reactions, 325–329
 - structure, 323–325
 - synthesis, 320–323
 - polynuclear alkylidyne complexes
 - reactions, 355–358
 - structure, 353–354
 - synthesis, 353, 355
 - anionic hydride complexes
 - as catalyst, 45–46
 - reactions, 28–30
 - with aldehydes, 42
 - with alkyl halides, 35–41
 - with Brønsted acids, 33–34
 - with Lewis acids, 31–33
 - with small electrophiles, 34
 - spectroscopic properties, 4–8, 23–27
 - structural characteristics, 12–13, 17–19
 - carbyne complexes
 - as catalyst, in alkene metathesis, 90
 - reactions
 - with acetylenes, 90–94
 - with acids, 78–81
 - with aldehydes, 102
 - with carbon monoxide, 99
 - carbyne cleavage, 97
 - carbyne coupling, 83–85
 - with cyclohexyl isocyanate, 101–102
 - with Lewis acids, 81–82
 - with metal complexes, 85–89
 - with methyl cyanate, 102
 - with nucleophiles, 71–77
 - with other tungsten carbynes, 101
 - photolysis, 98
 - with xylisocyanide, 98
 - spectroscopic properties, 56
 - structure, 54–55
 - synthesis, 57–60, 62–69
- mixed alkali metal compounds, 247, 251
- V**
- Vanadium
- anionic hydride complexes
 - reactions, 28–29
 - with acid halides, 41–42
 - with alkyl halides, 35–41
 - with small electrophiles, 34

Vanadium, anionic hydride complexes

(*cont.*)

spectroscopic properties, 4, 6, 23–25

structural characteristics, 11

mixed alkali metal compounds, 252

Vinylidenes, formation from transition

metal carbynes, 95–97

W

Water–gas shift reaction cycle, 1

Wittig chemistry, of tungsten alkoxides, 319–320

X

X-Ray crystallography, of organoplatinum(IV)

compounds, 122–123

X-Ray structural analysis, of alkali metal

organics, *see* Alkali metals,

organometallic complexes

Y

Ytterbium, mixed alkali metal compounds,
209

Yttrium, mixed alkali metal compounds,
215, 256

Z

Zeolite complexes, 236–238

Zinc

anionic hydride complexes, spectroscopic
properties, 6

carbyne complexes, reactions, with
acetylenes, 91

mixed alkali metal compounds, 219–220,
222, 247

Zirconium, mixed alkali metal compounds,
251

Cumulative List of Contributors

- Abel, E. W., 5, 1; 8, 117
 Aguilo, A., 5, 321
 Albano, V. G., 14, 285
 Alper, H., 19, 183
 Anderson, G. K., 20, 39
 Angelici, R. J., 27, 51
 Armitage, D. A., 5, 1
 Armor, J. N., 19, 1
 Ash, C. E., 27, 1
 Atwell, W. H., 4, 1
 Baines, K. M., 25, 1
 Barone, R., 26, 165
 Behrens, H., 18, 1
 Bennett, M. A., 4, 353
 Birmingham, J., 2, 365
 Blinka, T. A., 23, 193
 Bogdanović, B., 17, 105
 Bradley, J. S., 22, 1
 Brinckman, F. E., 20, 313
 Brook, A. G., 7, 95; 25, 1
 Brown, H. C., 11, 1
 Brown, T. L., 3, 365
 Bruce, M. I., 6, 273; 10, 273; 11, 447; 12, 379; 22, 59
 Brunner, H., 18, 151
 Buhro, W. E., 27, 311
 Cais, M., 8, 211
 Calderon, N., 17, 449
 Callahan, K. P., 14, 145
 Cartledge, F. K., 4, 1
 Chalk, A. J., 6, 119
 Chanon, M., 26, 165
 Chatt, J., 12, 1
 Chini, P., 14, 285
 Chisholm, M. H., 26, 97; 27, 311
 Chiusoli, G. P., 17, 195
 Churchill, M. R., 5, 93
 Coates, G. E., 9, 195
 Collman, J. P., 7, 53
 Connelly, N. G., 23, 1; 24, 87
 Connolly, J. W., 19, 123
 Corey, J. Y., 13, 139
 Corriu, R. J. P., 20, 265
 Courtney, A., 16, 241
 Coutts, R. S. P., 9, 135
 Coyle, T. D., 10, 237
 Craig, P. J., 11, 331
 Cullen, W. R., 4, 145
 Cundy, C. S., 11, 253
 Curtis, M. D., 19, 213
 Darensbourg, D. J., 21, 113; 22, 129
 Darensbourg, M. Y., 27, 1
 Deacon, G. B., 25, 237
 de Boer, E., 2, 115
 Deeming, A. J., 26, 1
 Dessy, R. E., 4, 267
 Dickson, R. S., 12, 323
 Eisch, J. J., 16, 67
 Emerson, G. F., 1, 1
 Epstein, P. S., 19, 213
 Erker, G., 24, 1
 Ernst, C. R., 10, 79
 Evans, J., 16, 319
 Evans, W. J., 24, 131
 Faller, J. W., 16, 211
 Faulks, S. J., 25, 237
 Fehlner, T. P., 21, 57
 Fessenden, J. S., 18, 275
 Fessenden, R. J., 18, 275
 Fischer, E. O., 14, 1
 Forster, D., 17, 255
 Fraser, P. J., 12, 323
 Fritz, H. P., 1, 239
 Furukawa, J., 12, 83
 Fuson, R. C., 1, 221
 Gallop, M. A., 25, 121
 Garrou, P. E., 23, 95
 Geiger, W. E., 23, 1; 24, 87
 Geoffroy, G. L., 18, 207; 24, 249
 Gilman, H., 1, 89; 4, 1; 7, 1
 Gladfelter, W. L., 18, 207; 24, 41
 Gladysz, J. A., 20, 1
 Green, M. L. H., 2, 325
 Griffith, W. P., 7, 211
 Grovenstein, Jr., E., 16, 167
 Gubin, S. P., 10, 347

- Guerin, C., 20, 265
 Gysling, H., 9, 361
 Haiduc, I., 15, 113
 Halasa, A. F., 18, 55
 Harrod, J. F., 6, 119
 Hart, W. P., 21, 1
 Hartley, F. H., 15, 189
 Hawthorne, M. F., 14, 145
 Heck, R. F., 4, 243
 Heimbach, P., 8, 29
 Helmer, B. J., 23, 193
 Henry, P. M., 13, 363
 Heppert, J. A., 26, 97
 Herberich, G. E., 25, 199
 Herrmann, W. A., 20, 159
 Hieber, W., 8, 1
 Hill, E. A., 16, 131
 Hoff, C., 19, 123
 Horwitz, C. P., 23, 219
 Housecroft, C. E., 21, 57
 Huang, Yaozeng (Huang, Y. Z.), 20, 115
 Ibers, J. A., 14, 33
 Ishikawa, M., 19, 51
 Ittel, S. D., 14, 33
 Jain, L., 27, 113
 Jain, V. K., 27, 113
 James, B. R., 17, 319
 Jolly, P. W., 8, 29; 19, 257
 Jonas, K., 19, 97
 Jones, M. D., 27, 279
 Jones, P. R., 15, 273
 Jukes, A. E., 12, 215
 Jutzi, P., 26, 217
 Kaesz, H. D., 3, 1
 Kaminsky, W., 18, 99
 Katz, T. J., 16, 283
 Kawabata, N., 12, 83
 Kemmitt, R. D. W., 27, 279
 Kettle, S. F. A., 10, 199
 Kilner, M., 10, 115
 Kim, H. P., 27, 51
 King, R. B., 2, 157
 Kingston, B. M., 11, 253
 Kitching, W., 4, 267
 Köster, R., 2, 257
 Kreiter, C. G., 26, 297
 Krüger, G., 24, 1
 Kudasoski, R. A., 22, 129
 Kühlejn, K., 7, 241
 Kuivila, H. G., 1, 47
 Kumada, M., 6, 19; 19, 51
 Lappert, M. F., 5, 225; 9, 397; 11, 253; 14, 345
 Lawrence, J. P., 17, 449
 Lednor, P. W., 14, 345
 Longoni, G., 14, 285
 Luijten, J. G. A., 3, 397
 Lukehart, C. M., 25, 45
 Lupin, M. S., 8, 211
 McKillop, A., 11, 147
 Macomber, D. W., 21, 1; 25, 317
 Maddox, M. L., 3, 1
 Maitlis, P. M., 4, 95
 Mann, B. E., 12, 135
 Manuel, T. A., 3, 181
 Mason, R., 5, 93
 Masters, C., 17, 61
 Matsumura, Y., 14, 187
 Mingos, D. M. P., 15, 1
 Mochel, V. D., 18, 55
 Moedritzer, K., 6, 171
 Morgan, G. L., 9, 195
 Mrowca, J. J., 7, 157
 Müller, G., 24, 1
 Mynott, R., 19, 257
 Nagy, P. L. I., 2, 325
 Nakamura, A., 14, 245
 Nesmeyanov, A. N., 10, 1
 Neumann, W. P., 7, 241
 Ofstead, E. A., 17, 449
 Ohst, H., 25, 199
 Okawara, R., 5, 137; 14, 187
 Oliver, J. P., 8, 167; 15, 235; 16, 111
 Onak, T., 3, 263
 Oosthuizen, H. E., 22, 209
 Otsuka, S., 14, 245
 Pain, G. N., 25, 237
 Parshall, G. W., 7, 157
 Paul, I., 10, 199
 Petrosyan, W. S., 14, 63
 Pettit, R., 1, 1
 Pez, G. P., 19, 1
 Poland, J. S., 9, 397
 Poliakoff, M., 25, 277
 Popa, V., 15, 113
 Pourreau, D. B., 24, 249
 Powell, P., 26, 125
 Pratt, J. M., 11, 331
 Prokai, B., 5, 225
 Pruett, R. L., 17, 1
 Rao, G. S., 27, 113
 Rausch, M. D., 21, 1; 25, 317

- Reetz, M. T., **16**, 33
 Reutov, O. A., **14**, 63
 Rijkens, F., **3**, 397
 Ritter, J. J., **10**, 237
 Rochow, E. G., **9**, 1
 Roper, W. R., **7**, 53; **25**, 121
 Roundhill, D. M., **13**, 273
 Rubezhov, A. Z., **10**, 347
 Salerno, G., **17**, 195
 Satgé, J., **21**, 241
 Schade, C., **27**, 169
 Schmidbaur, H., **9**, 259; **14**, 205
 Schrauzer, G. N., **2**, 1
 Schulz, D. N., **18**, 55
 Schwebke, G. L., **1**, 89
 Setzer, W. N., **24**, 353
 Seyferth, D., **14**, 97
 Shen, Yanchang (Shen, Y. C.), **20**, 115
 Shirver, D. F., **23**, 219
 Siebert, W., **18**, 301
 Sikora, D. J., **25**, 317
 Silverthorn, W. E., **13**, 47
 Singleton, E., **22**, 209
 Sinn, H., **18**, 99
 Skinner, H. A., **2**, 49
 Slocum, D. W., **10**, 79
 Smith, J. D., **13**, 453
 Speier, J. L., **17**, 407
 Stafford, S. L., **3**, 1
 Stone, F. G. A., **1**, 143
 Su, A. C. L., **17**, 269
 Suslick, K. M., **25**, 73
 Swincer, A. G., **22**, 59
 Tamao, K., **6**, 19
 Tate, D. P., **18**, 55
 Taylor, E. C., **11**, 147
 Thayer, J. S., **5**, 169; **13**, 1; **20**, 313
 Theodosiou, I., **26**, 165
 Timms, P. L., **15**, 53
 Todd, L. J., **8**, 87
 Treichel, P. M., **1**, 143; **11**, 21
 Tsuji, J., **17**, 141
 Tsutsui, M., **9**, 361; **16**, 241
 Turney, T. W., **15**, 53
 Tyfield, S. P., **8**, 117
 Vahrenkamp, H., **22**, 169
 van der Kerk, G. J. M., **3**, 397
 van Koten, G., **21**, 151
 Vezey, P. N., **15**, 189
 von Ragué Schleyer, P., **24**, 353; **27**, 169
 Vrieze, K., **21**, 151
 Wada, M., **5**, 137
 Walton, D. R. M., **13**, 453
 Wailles, P. C., **9**, 135
 Webster, D. E., **15**, 147
 Weitz, E., **25**, 277
 West, R., **5**, 169; **16**, 1; **23**, 193
 Werner, H., **19**, 155
 Wiberg, N., **23**, 131; **24**, 179
 Wiles, D. R., **11**, 207
 Wilke, G., **8**, 29
 Wojcicki, A., **11**, 87; **12**, 31
 Yashina, N. S., **14**, 63
 Ziegler, K., **6**, 1
 Zuckerman, J. J., **9**, 21